On the k-Independent Subsets of the Euclidean Space and of the Hilbert Space

by

K. BORSUK

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1. For every ordinal $\alpha \leqslant \omega$ let us denote by E_α the α-dimensional Euclidean space, if α is finite, and the Hilbert space *), if $\alpha = \omega$. Let k be a natural. We shall say that a subset A of E_α is *k-independent* if every subset of A containing $\leqslant k+2$ points is linearly independent. A subset A of E_α which is k-independent for every $k = 1, 2$ will be said to be *ω-independent*.

2. THEOREM. *Let X be a separable metric space. The set of homeomorphisms of X onto ω-independent subsets of the Hilbert cube Q_ω **) is dense in the space Q_ω^X ***) of all continuous mappings of X in Q_ω.*

Proof. Let f be a continuous mapping of X in Q_ω. By the imbedding theorem of Urysohn ([5], also [2], p. 64) there exists for every $0 < \varepsilon < 1$ a homeomorphism $g \in Q_\omega^X$ such that

(1) $\varrho(f(x), g(x)) < \tfrac{1}{3}\varepsilon$ for every point $x \in X$.

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*) *Hilbert-space* E_ω = space of real-valued sequences $\{x_1, x_2, ...\}$, for which $\sum\limits_{n=1}^{\infty} x_n^2$ is finite. It is metrised by the formula

$$\varrho(\{x_1, x_2, ...\},\ \{y_1, y_2, ...\}) = \sqrt{\sum_{n=1}^{\infty} (x_n - y_n)^2}.$$

**) *Hilbert-cube* Q_ω = set of points $\{x_1, x_2, ...\} \in E_\omega$ satisfying the inequalities $|x_n| \leqslant \dfrac{1}{n}$ for every $n = 1, 2, ...$

***) Q_ω^X denotes the set of all continuous mappings of X in Q_ω metrised by the formula $\varrho(f, g) = \sup\limits_{x \in X} \varrho(f(x), g(x))$.

Let n_0 be a natural such that

$$(2) \qquad \sum_{n=n_0+1}^{\infty} \frac{1}{n^2} < \frac{1}{10}\varepsilon^2.$$

Consider the mapping $\varphi \in Q_\omega^{Q_\omega}$ defined by the formula

$$(3) \qquad \varphi(\{y_1, y_2, \ldots, y_n, \ldots\}) = \{y_1, \ldots, y_{n_0}, 0, \tfrac{1}{3}y_{n_0+1}, 0, \tfrac{1}{3}y_{n_0+2}, 0, \ldots\}.$$

Evidently, φ is a homeomorphism, mapping Q_ω into itself and satisfying, by (2), the inequality

$$(4) \qquad \varrho(y, \varphi(y)) < \tfrac{1}{3}\varepsilon \qquad \text{for every point } y \in Q_\omega.$$

Consider now a countable basis U for Q_ω, i.e., a sequence $U_1, U_2, \ldots, U_k, \ldots$ of open subsets of Q_ω such that every open subset of Q_ω is the sum of some sets U_k. Manifestly there exists for every $k = 1, 2, \ldots$ a real-valued, continuous function ψ_k defined on Q_ω and satisfying the following conditions:

$$(5) \qquad 0 < \psi_k(y) < \tfrac{1}{3}\varepsilon, \qquad \text{for every point} \quad y \in U_k,$$

$$(6) \qquad \psi_k(y) = 0, \qquad \text{for every point} \quad y \in Q_\omega - U_k.$$

Let us now denote by d_k the point $\{x_1, x_2, \ldots\} \in E_\omega$ with all coordinates x_ν vanishing except the coordinate x_k equal to 1. Setting

$$(7) \qquad \psi(y) = \varphi(y) + \sum_{k=1}^{\infty} \frac{\psi_k(y)}{n_0 + 2k - 1} \cdot d_{n_0+2k-1},$$

we obtain by (3) a mapping $\psi \in Q_\omega^{Q_\omega}$ satisfying, by (2), (5) and (7), the inequality

$$(8) \qquad \varrho(\varphi(y), \psi(y)) < \tfrac{1}{3}\varepsilon \qquad \text{for every point} \quad y \in Q_\omega.$$

It follows from (3) and (7) that the coordinates of the point $\varphi(y)$ are determined by the coordinates of the point $\psi(y)$. Hence the mapping ψ is univalent. Since Q_ω is compact we infer that ψ is a homeomorphism and consequently the mapping ψg of the space X into Q_ω is also a homeomorphism. Moreover, it follows by (1), (4) and (8) that for every point $x \in X$ we have

$$\varrho(f(x), \psi g(x)) \leqslant \varrho(f(x), g(x)) + \varrho(g(x), \varphi g(x)) + \varrho(\varphi g(x), \psi g(x)) < \varepsilon.$$

It remains to be shown that for every finite sequence $x_1, x_2, \ldots, x_m$ of different points of X the points $\psi g(x_1), \psi g(x_2), \ldots, \psi g(x_m)$ are linearly independent. Since g is a homeomorphism, the points $g(x_1), g(x_2), \ldots, g(x_m)$ are different. It follows that in the basis U there exist disjoint sets

$U_{k_1}, U_{k_2}, ..., U_{k_m}$ such that

(9) $$g(x_\nu) \in U_{k_\nu} \quad \text{for} \quad \nu = 1, 2, ..., m.$$

We infer by (5), (6) and (7) that the $(n_0 + 2k_\nu - 1)$-th coordinate of the point $\psi g(x_\nu)$ is positive, while the same coordinate of the points $\psi g(x_\mu)$, where $\mu \neq \nu$, vanishes. Hence, the points $\psi g(x_1), \psi g(x_2), ..., \psi g(x_m)$ are linearly independent.

3. Consider now some examples of k-independent subsets of Euclidean spaces:

EXAMPLE 1. Let S_{n-1} denote an $(n-1)$-dimensional geometrical sphere lying in the space E_n. Since no three points of S_{n-1} lie on a straight line, S_{n-1} is 1-independent. Combining this remark with the imbedding theorem of Menger and Nöbeling ([2], p. 56) we infer that every m-dimensional separable metric space is homeomorphic with a 1-independent subset of E_{2m+2}.

EXAMPLE 2. Consider the homeomorphism φ mapping the straight line E_1 onto a subset of E_{k+1} given by the formula

$$\varphi(t) = (t, t^2, ..., t^{k+1}) \text{ for every } \quad (t) \in E_1.$$

Let $\varphi(t_0), \varphi(t_1), ..., \varphi(t_{k+1})$ be $k+2$ different points of $\varphi(E_1)$. Then the determinant of Vandermonde with the rows $1, t_\nu, ..., t_\nu^{k+1}$ is different from 0. We conclude that the points $\varphi(t_0), \varphi(t_1), ..., \varphi(t_{k+1})$ are linearly independent. It follows that every linear set (in particular, every 0-dimensional separable metric space) is homeomorphic with a k-independent subset of E_{k+1}.

EXAMPLE 3. Let ϱ and ϑ be the polar coordinates in the plane E_2. Setting

$$f(\varrho, \vartheta) = (\varrho \cos \vartheta, \varrho \sin \vartheta, \varrho^2 \cos 2\vartheta, \varrho^2 \sin 2\vartheta, ..., \varrho^{k+1} \cos(k+1)\vartheta, \varrho^{k+1} \sin(k+1)\vartheta)$$

for every $\varrho \geqslant 0$ and every real ϑ, we obtain a homeomorphism f mapping E_2 onto a subset $f(E_2)$ of the space E_{2k+2}.

Let $f(\varrho_0, \vartheta_0), f(\varrho_1, \vartheta_1), ..., f(\varrho_{k+1}, \vartheta_{k+1})$ be a system of $k+2$ different points of $f(E_2)$. In order to prove that they are linearly independent it suffices to show that the rank of the matrix with $k+2$ rows of the form

$$1, \quad \varrho_\nu \cos \vartheta_\nu, \varrho_\nu \sin \vartheta_\nu, \varrho_\nu^2 \cos 2\vartheta_\nu, \varrho_\nu^2 \sin 2\vartheta_\nu, ..., \varrho_\nu^{k+1} \cos(k+1)\vartheta_\nu, \varrho_\nu^{k+1} \sin(k+1)\vartheta_\nu,$$

with $\nu = 0, 1, ..., k+1$ is equal to $k+2$. This rank will not be changed if we multiply the third column by $i = \sqrt{-1}$ and add it to the second, multiply the fifth column by i and add it to the fourth and so on. Setting

$$z_\nu = \varrho_\nu \cdot (\cos \vartheta_\nu + i \sin \vartheta_\nu) \quad \text{for} \quad \nu = 0, 1, ..., k+1,$$

we see at once that the matrix obtained in this manner contains the determinant of Vandermonde with the rows $1, z_\nu, z_\nu^2, ..., z_\nu^{k+1}$, where $\nu = 0, 1, ..., k+1$. Since $z_\mu \neq z_\nu$ for $\mu \neq \nu$, this determinant does not vanish. Hence the set $f(E_2)$ is k-independent.

It follows that every plane set is homeomorphic with a k-independent subset of E_{2k+2}.

EXAMPLE 4. Let K denote a simple closed curve lying in E_3. Consider three points, $a_1, a_2, a_3 \in K$, cutting K into three simple open arcs: K_1 with the endpoints a_2, a_3, K_2 with the endpoints a_1, a_3 and K_3 with the endpoints a_1, a_2. Let P be a plane passing by a_1, a_2, a_3. If P does not contain four different points of K, then each of the open arcs K_1, K_2, K_3 lies on one side of P. Then two of them, for instance K_1, K_2, lie on the same side of P. Consider a point $b_1 \in K_1$, a point $b_2 \in K_2$ and a plane P' parallel to P and such that a_1, a_2, a_3 lie on one side of P' and b_1, b_2 — on the other. It follows that P' cuts each of the arcs K_1 and K_2 in at least two points; hence P' contains at least four different points of K. Thus we have shown that no simple closed curve lying in E_3 is 2-independent.

The following example (due to M. Fiedler) shows that in E_4 there exist 2-independent simple closed curves. Setting

$$f(t) = (\cos^3 t . \sin t, \ \cos^2 t \cdot \sin^2 t, \ \cos t \cdot \sin^3 t, \ \sin^4 t) \text{ for } 0 \leqslant t < \pi,$$

we obtain a parametric representation of a simple closed curve in E_3. In order to prove that it is 2-independent it suffices to show that for every system of numbers $0 \leqslant t_1 < t_2 < t_3 < t_4 < \pi$ the rank of the matrix with the rows:

$$1, \ \cos^3 t_\nu \cdot \sin t_\nu, \ \cos^2 t_\nu \cdot \sin^2 t_\nu, \ \cos t_\nu \cdot \sin^3 t_\nu, \ \sin^4 t_\nu,$$

$\nu = 1, 2, 3, 4$ is equal to 4. If $t_1 = 0$, then the determinant obtained by cancelling the second column is equal to the product of the term $\sin^4 t_2 \cdot \sin^4 t_3 \cdot \sin^4 t_4 \neq 0$ and of the determinant of Vandermonde with the rows: $\operatorname{ctg}^2 t_\nu, \operatorname{ctg} t_\nu, 1$, where $\nu = 2, 3, 4$. Since $\operatorname{ctg} t_\mu \neq \operatorname{ctg} t_\nu$, for $\mu \neq \nu$, this determinant is $\neq 0$. If however $t_1 > 0$, then the determinant obtained by cancelling the first column in the matrix is equal to the product of the term $\sin^4 t_1 \cdot \sin^4 t_2 \cdot \sin^4 t_3 \cdot \sin^4 t_4 \neq 0$ and of the determinant of Vandermonde with the rows: $\operatorname{ctg}^3 t_\nu, \operatorname{ctg}^2 t_\nu, \operatorname{ctg} t_\nu, 1$, where $\nu = 1, 2, 3, 4$. Since for $\mu \neq \nu$, $\operatorname{ctg} t_\mu \neq \operatorname{ctg} t_\nu$, this determinant is $\neq 0$.

4. Let X be a metric separable space and α an ordinal $\leqslant \omega$. By the theorem in **2** there exist ordinals $\beta \leqslant \omega$ such that X is homeomorphic with an α-independent subset of E_β. Let us denote by $D_k(X)$ the minimal of such ordinals β. Evidently,

(10) $\quad X_1 \subset X_2 \quad$ implies $\quad D_k(X_1) \leqslant D_k(X_2) \quad$ for every $\quad k = 1, 2, \ldots,$

(11) $\quad\quad k_1 < k_2 \quad$ implies $\quad D_{k_1}(X) \leqslant D_{k_2}(X) \quad$ for every $\quad X.$

By example 1 we have

(12) $$D_1(S_{n-1}) = n$$

and by example 2

(13) $$D_k(E_1) \leqslant k+1.$$

Example 3 yields the inequality

(14) $$D_k(E_2) \leqslant 2k + 2.$$

Finally, by example 4 we have

(15) $$D_2(S_1) = 4.$$

Moreover, let us observe that (10) and the imbedding theorem of Menger and Nöbeling ([2], p. 56) give the following inequality:

(16) $$\text{If} \quad \dim X \leqslant n, \quad \text{then} \quad D_k(X) \leqslant D_k(E_{2n+1}).$$

It would be interesting to calculate the value of $D_k(X)$ for some more general classes of spaces X. Even the question whether $D_k(E_n)$ is finite for all natural k and n finite seems to be open. The positive answer to this question would imply, by (16), the finiteness of $D_k(X)$ for all finite dimensional, separable, metric spaces X.

5. We shall now establish some elementary properties of the k-independent subsets of E_n.

Theorem. *Let A be a k-independent compact subset of E_n. Then for every open set U containing at least k points of A the set $A - U$ is homeomorphic with a subset of E_{n-k}.*

Proof. Consider a system $a_1, a_2, \ldots, a_k$ of k different points of $A \cap U$. Since A is k-independent, there exists exactly one $(k-1)$-dimensional hyperplane $H_{k-1} \subset E_n$ containing all the points $a_1, a_2, \ldots, a_k$. Moreover, for every point $x \in A - U$ there exists exactly one k-dimensional hyperplane $H_k(x) \subset E_n$ spanned by the points $a_1, a_2, \ldots, a_k, x$. We have

(17) $$H_k(x) \cap (A - U) = (x) \quad \text{for every} \quad x \in A - U.$$

Let P denote the $(n-k+1)$-dimensional hyperplane in E_n passing through a_1 and orthogonal to H_{k-1}, and let S_{n-k} denote an $(n-k)$-dimensional geometrical sphere lying in P and passing through a_1. It is easy to see that for every point $x \in A - U$ the hyperplane $H_k(x)$ meets $S_{n-k} - (a_1)$ in exactly one point $\varphi(x)$ depending continuously on x. Moreover, by (17), the function φ assigns different values to different points x of the compact set $A - U$. Hence, φ maps the set $A - U$ topologically onto a subset of the set $S_{n-k} - (a_1)$. Since $S_{n-k} - (a_1)$ is homeomorphic with E_{n-k}, our proof in finished.

Corollary 1. *If A is a 1-independent compact subset of E_n, then every closed, proper subset of A is homeomorphic with a subset of E_{n-1}.*

Corollary 2. *If A is a k-independent compact subset of E_n containing no isolated points, then every closed proper subset of A is homeomorphic with a subset of E_{n-k}.*

Corollary 3. *For every natural k and m there exists an m-dimensional polytope which is not homeomorphic with any k-independent subset of E_{2m+k}.*

Proof. Consider an m-dimensional polytope Q which is not homeomorphic with any subset of E_{2m} (see [1]) and let A denote the union of Q and of a segment L disjoint to Q. By Corollary 2, the set A is not homeomorphic with any k-independent subset of E_{2m-k}.

6. Theorem. *Every k-independent compact subset A of E_n is homeomorphic with a subset of E_{n-k+2}.*

Proof. If $k < 2$, then the statement is trivial. Suppose that $k \geqslant 2$. Consider a system $a_1, a_2, \ldots, a_k$ of k different points of A. Since A is k-independent, there exists exactly one $(k-1)$-dimensional hyperplane $H_{k-1} \subset E_n$ spanned by the points $a_1, a_2, \ldots, a_k$. Then

$$A \cap H_{k-1} = (a_1, a_2, \ldots, a_k).$$

Consider a $(k-2)$-dimensional hyperplane $H_{k-2} \subset H_{k-1}$ such that none of the vectors $\overrightarrow{a_\mu a_\nu}$, $\mu, \nu = 1, 2, \ldots, k$; $\mu \neq \nu$, is parallel to H_{k-2}. Let P_{n-k+2} be an $(n-k+2)$-dimensional hyperplane in E_n orthogonal to H_{k-2}, and let x be a point of A. Let us denote by $H_{k-2}(x)$ the $(k-2)$-dimensional hyperplane containing x and parallel to H_{k-2}. Evidently $H_{k-2}(x)$ intersects P_{n-k+2} at exactly one point. Denoting this point by $\varphi(x)$, we obtain a function φ mapping A onto a subset of P_{n-k+2}. Since φ is manifestly continuous, it remains to be shown that

$$\varphi(x) \neq \varphi(y) \quad \text{if} \quad x, y \, \epsilon \, A \quad \text{and} \quad x \neq y.$$

Suppose this is not true. Then the points x, y lie on a $(k-2)$-dimensional hyperplane $\overset{*}{H}_{k-2}$ parallel to H_{k-2}. By our assumption concerning the hyperplane H_{k-2} it is impossible that x or y belong to the system $a_1, a_2, \ldots, a_k$. If, however, x and y do not belong to the system $a_1, a_2, \ldots, a_k$, then the $k+2$ points $x, y, a_1, a_2, \ldots, a_k$ are different and they lie on the k-dimensional hyperplane passing through x and containing H_{k-1}. But this is impossible, because A is k-independent.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

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Some Characterisation of the Brown-McCoy Radical

by

A. SULIŃSKI

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Let us recall at the beginning the fundamental concepts of the general theory of radicals (see [1] and [4]).

Let K be a class of rings with the property that the homomorphic image of a ring from K and an ideal of a ring from K are in K.

If P is a property of certain rings from K, then a ring which possesses property P is called a *P-ring*, and every ideal of $R \in K$, which is a P-ring, is called *P-ideal*. If in the ring $R \in K$ there exists a P-ideal $P(R)$ containing all P-ideals of R, then $P(R)$ is called a *P-radical of R*. A ring without non-zero P-ideals is called *P-semi-simple*.

A *P-radical is defined in the class K*, if property P satisfies the following conditions:

(a) the homomorphic image of a P-ring is a P-ring;

(b) in every ring $R \in K$ there exists a P-radical $P(R)$;

(c) $R/P(R)$ is P-semi-simple.

If property P satisfies these conditions, then P-rings are called *P-radical rings*.

We note one more condition of P:

(d) all ideals of a P-ring are P-ideals.

Let K_S be a class of all simple rings from K. It has been proved in [4] that every P-radical defined in K decomposes class K_S into two classes: a class of all simple P-semi-simple rings *(upper class K_U)*, and a class of all simple P-radical rings *(lower class K_L)*. The intersection $K_U \cap K_L = 0$. Inversely, if we have a decomposition of K_S in the upper class K_U and in the lower class K_L, such that $K_U \cap K_L = 0$, then in general many radicals correspond to this decomposition, but all these radicals are contained between the *upper U and the lower L radicals of this decomposition*.

It is known (see [1] and [4]) that a subdirect sum of semi-simple rings is semi-simple. Professor A. G. Kurosh has formulated the fol-

lowing problem: Under what conditions is every U-semi-simple ring a subdirect sum of simple rings from K? We shall call decompositions of K_S possessing this property, *faithful decompositions* and upper radicals corresponding to these decompositions, *faithful radicals*.

If K is a class of all associative rings with a certain domain *) of operators, then we have the following theorems.

THEOREM 1. *If the decomposition of K_S in the upper class K_U and the lower class K_L is such that in K_U there are no simple rings not containing unity, then U is a faithful radical.*

THEOREM 2. *If the decomposition of K_S is as above, then radical U satisfies* (d).

If the class K_S consists of all simple rings containing unity, then from Theorem 1 we obtain the well known theorem of Brown and McCoy [2]. The property (d) for the Brown-McCoy radical was established in [3].

If K is a class of all associative rings without a domain of operators, then the following theorem will be a conversion to Theorems 1 and 2.

THEOREM 3. *If the decomposition of K_S in the upper class K_U and the lower class K_L is faithful and the radical U satisfies* (d), *then in the class K_U there are no simple rings not containing unity.*

Theorem 3 is also true in the class of all associative algebras over the field Φ.

If K is a class of all non-associative algebras over the field Φ, then the following theorem is true.

THEOREM 4. *If the decomposition of K_S in the upper class K_U and the lower class K_L is faithful, then in the upper class K_U there are no simple algebras not containing unity.*

The converse theorem to Theorem 4 is the following statement: If the decomposition of class K_S is such, that in the upper class K_U there are no simple algebras not containing unity, then this is a faithful decomposition. In the case where the class K_U consists of all simple rings containing unity, this statement has been proved in [5]. In the general cases, the question is still open.

The proofs of these results will be published in Matematichesky Sbornik.

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LOMONOSOV UNIVERSITY, MOSCOW

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*) We assume that all the rings from K have the same domain of operators.

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Radicals in Associative Algebras of Finite Order

by

A. SULIŃSKI

In [1] and [2] were developed the beginnings of the general theory of radicals. We recall the fundamental notions.

Let K be a class of rings in which the following conditions are satisfied:

(1) the homomorphic image of a ring from K belongs to K;

(2) all ideals of the ring from K belong to K.

Let P denote a property of certain rings from K. By a *P-ring* we mean a ring which possesses property P. The ideal of a ring $R \in K$, which is a P-ring, will be called *P-ideal*. If the ring $R \in K$ possesses a P-ideal $P(R)$ which contains all P-ideals of R, then $P(R)$ is called the *P-radical of R*. A ring without non-zero P-ideals is a *P-semi-simple* ring.

A *P-radical is defined in the class* K, if property P satisfies the following conditions:

(a) the homomorphic image of a P-ring is a P-ring;

(b) in each ring $R \in K$ there exists a P-radical $P(R)$;

(c) the factor ring $R/P(R)$ is P-semi-simple.

If property P satisfies conditions (a), (b) and (c), then P-rings are called *P-radical rings*. It is known that the conditions (a), (b), (c) in [2] are equivalent to the conditions (A), (B), (C) in [1].

Condition (a) implies that one element zero-ring is a P-ring. Hence a P-semi-simple ring can be defined as a ring, the P-radical of which is zero.

We note one more condition of P:

(d) all ideals of a P-ring are P-ideals.

A radical S defined in K will be called the *antiradical* of radical P (also defined in K), if every S-radical ring is P-semi-simple. If radical P satisfies condition (d), then P is also an antiradical of S. Indeed, if R is a P-radical ring, then $S(R) = 0$, because, if this were not so, R would

contain a non-zero P-semi-simple ideal $S(R)$. But this is impossible under condition (d).

S is a *maximal antiradical* of a radical P, if there is no antiradical of P properly containing S. If S is a maximal antiradical of P and P is a maximal antiradical of S, then (P, S) will be called *a pair of maximal antiradicals*.

Let K_S be a class of all simple rings from K. In [2] it was proved that each P-radical defined in K, decomposes class K_S into two classes: a class of all simple P-semi-simple rings *(upper class K_U)*, and a class of all simple P-radical rings *(lower class K_L)*. The intersection $K_U \cap K_L = 0$. Conversely, if we have a decomposition of K_S in the upper class K_U and in the lower class K_L, such that $K_U \cap K_L = 0$, then in general many radicals correspond to this decomposition, but all these radicals are contained between the *upper U and the lower L radicals of this decomposition*. R is a U-radical ring if, and only if, there exists no homomorphic mapping of R onto the simple ring from K_U. The lower radical L is constructed in the following manner. Let K_L^* be the class of all rings such that every non-zero homomorphic image contains a non-zero ideal which, as a ring, belongs to K_L. By transfinite induction we can define

$K_0 = K_L,$

$K_a = K_{a-1}^*,$ if $a - 1$ exists,

$K_a = \bigcup_{\xi < a} K_\xi,$ if a is a limit ordinal.

R is an L-radical ring if, and only if, there exists an ordinal a such that $R \in K_a$ [2].

Now let K be the class of all associative algebras of finite order over the field Φ. Class K_S consists of a zero algebra of order one, which will be denoted by Z, and of total matric algebras over the division algebras. The object of this paper is to give a survey of the radicals in K. Here we shall find the following two different cases: (I) Z is a radical algebra, and (II) Z is a semi-simple algebra.

THEOREM 1. *If the decomposition of K_S in the upper class K_U and the lower class K_L is such that $Z \in K_L$, then $U = L$, i. e., to this decomposition corresponds only one radical.*

This theorem can be generalised to the class of algebras over Φ with the property that its finitely generated ideals are of finite order over Φ. Hence it follows, in particular, that in this class the lower Baer radical, the locally nilpotent radical, the Jacobson radical and the Brown-McCoy radical all coincide.

We now assume that algebra Z belongs to K_U and that all the rest of the simple algebras belong to K_L. Then we have

THEOREM 2. *A is a U-radical algebra if, and only if, $A^2 = A$.*

THEOREM 3. *A is an L-radical algebra if, and only if, A is W-semi-simple, where W is a classical nilpotent radical.*

COROLLARY 1. *Radicals L and W constitute a pair of maximal anti-radicals.*

Radical L does not coincide with U.

THEOREM 4. *Class T of all algebras containing unity is a radical class. The radical T is properly contained between L and U.*

Let M be a class of all directly irreducible algebras containing unity. We shall call a subset N of the set M a *closed class of directly irreducible algebras containing unity*, if N satisfies the condition:

(g) Every directly irreducible homomorphic image of an algebra from N belongs to N.

If N is a closed class of directly irreducible algebras containing unity, then by $S(N)$ we shall denote all finite direct sums of algebras from N.

THEOREM 5. *If P is a radical class contained in T, then $P \cap M$ is a closed class of directly irreducible algebras containing unity, and $S(P \cap M) = P$.*

THEOREM 6. *If N is a closed class of directly irreducible algebras containing unity, then $S(N)$ is a radical class contained in T.*

Theorem 5 and 6 establish a one-to-one correspondence between the radicals contained in T and the closed classes of directly irreducible algebras containing unity. In this correspondence, to each closed class N corresponds the radical $S(N)$.

THEOREM 7. *In class K condition* (d) *is satisfied by all radicals of decompositions of K_S in which Z is a radical algebra, and by all lower radicals of decompositions in which Z is a semi-simple algebra. No other radicals in K satisfy condition* (d).

If K is a *class of all associative commutative algebras* of finite order over the field Φ, then Theorems 1, 5 and 6 describe all the radicals in K, because in this case the class of all idempotent algebras coincides with the class of all algebras containing unity.

The proofs of these results will be published in Matematichesky Sbornik.

The author is greatly indebted to Professor A. G. Kurosh, under whose guidance he wrote this paper during his study stage in the USSR.

LOMONOSOV UNIVERSITY, MOSCOW

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On the Approximate Solution of Linear Algebraic Equations

by

M. ALTMAN

In the present paper we give an approximate method for solving linear algebraic equations. This method has a very simple geometrical sense. A similar method is given by Kaczmarz [2]. The method of Kaczmarz has also a geometrical sense and the constructions of both methods are based on the orthogonal projection. But the geometrical sense of Kaczmarz's method is directly connected with considering each separate equation of the system as a certain plane and therefore cannot be formulated in a more abstract form.

1. Let X be a n-dimensional linear space with a scalar product (u,v) of vectors $u,v \in X$, and let A be a linear transformation of X into itself. We suppose that A is one-to-one. Consider the linear equation

$$(1) \qquad Ax = b, \qquad (x, b \in X).$$

Let e_i $(i = 1, 2, ..., n)$ be an arbitrary basis in X. Denote by P_i the orthogonal projection on the vector Ae_i $(i = 1, 2, ..., n)$. Define the infinite sequence of vectors as follows:

$$y_1 = b - P_1 b, \qquad y_2 = y_1 - P_2 y_1 \qquad ,..., \qquad y_n = y_{n-1} - P_n y_{n-1},$$

$$y_{n+1} = y_n - P_1 y_n, \qquad y_{n+2} = y_{n+1} - P_2 y_{n+1} \qquad ,...,$$

$$(2) \qquad y_{n+i} = y_{n+i-1} - P_i y_{n+i-1} \qquad (\text{for } i = 1, 2, ..., n),$$

$$y_{2n+1} = y_{2n} - P_1 y_{2n} \qquad ,..., \qquad y_{jn+i} = y_{jn+i-1} - P_i y_{jn+i-1}$$

$$(\text{for } i = 1, 2, ..., n; \ j = 1, 2, ...), ...$$

We shall show that the sequence $\{y_k\}$ converges to the null-vector. In fact, we have evidently

$$(3) \qquad \|y_{k+1}\|^2 = \|y_k\|^2 - \|P_{i_k} y_k\|^2,$$

or

$$\|y_{k+1}\|^2 = \|y_k\|^2 - \frac{(y_k, Ae_{i_k})^2}{\|Ae_{i_k}\|^2},$$

since $\quad P_l y = \dfrac{(y, Ae_l)}{\|Ae_l\|^2} Ae_l \quad$ ($\|y\|$ denotes the norm of y).

It follows by (3) that the sequence $\{\|y_k\|^2\}$ is monotonously decreasing and therefore also convergent. In order to prove that $y_k \to 0$ as $k \to \infty$ it is sufficient to show the existence of a subsequence of $\{y_k\}$ which converges to the null-vector. It follows from (3) that the sequence $\{\|P_{i_k} y_k\|^2\}$ converges to zero. Now let us consider the subsequence of $\{y_k\}$ corresponding to projection P_1; since it is bounded there exists a subsequence $\{y_{k_p}\}$ which converges to a certain vector u.

Since this subsequence corresponds to projection P_1, we have

$$y_{k_p+1} = y_{k_p} - \frac{1}{\|Ae_1\|^2}(y_{k_p}, Ae_1) Ae_1$$

and

$$(y_{k_p}, Ae_1) \to 0 \quad \text{as} \quad p \to \infty.$$

Hence, we obtain $(u, Ae_1) = 0$.

It is easy to see by (2), (3) and using the above-mentioned properties of the subsequence $\{y_{k_p}\}$ that

$$y_{k_p+l+1} = y_{k_p+l} - \frac{1}{\|Ae_{l+1}\|^2}(y_{k_p+l}, Ae_{l+1}) Ae_{l+1},$$

$$(y_{k_p+l}, Ae_{l+1}) \to 0 \quad \text{as} \quad p \to \infty,$$

$$y_{k_p+l} \to u \quad \text{as} \quad p \to \infty,$$

for $i = 0, 1, \ldots, n-1$. Thus, we obtain $(u, Ae_i) = 0$ for $i = 1, 2, \ldots, n$. Since $\{e_i\}$ is a basis in X, and A is one-to-one, we infer that u is the null-vector.

We are now in a position to construct the approximate solution of Eq. (1). Put

(4)
$$w_1 = \frac{1}{\|Ae_1\|^2}(b, Ae_1)e_1, \quad w_2 = \frac{1}{\|Ae_2\|^2}(y_1, Ae_2)e_2, \ldots,$$

$$w_k = \frac{1}{\|Ae_{i_k}\|^2}(y_{k-1}, Ae_{i_k})e_{i_k},$$

i. e., the vector w_k is obtained by replacing in the projection P_{i_k} the corresponding vector Ae_{i_k} by e_{i_k}. Hence, we have $Aw_1 = P_1 b$, $Aw_2 = P_2 y_1, \ldots,$ $Aw_k = P_{i_k} y_{k-1}$, where vectors y_k $(k = 1, 2, \ldots)$ are defined by (2). The approximate solution x_k is defined by the formula

$$(5) \qquad x_k = w_1 + w_2 + \ldots + w_k,$$

where w_k is defined by (4).

We shall show that the approximate solution x_k converges to the solution of Eq. (1). In fact, we have by (2)

$$P_1 b = b - y_1, \qquad P_2 y_1 = y_1 - y_2, \ldots, \qquad P_{i_k} y_{k-1} = y_{k-1} - y_k.$$

Hence, adding these equations we obtain

$$P_1 b + P_2 y_1 + \ldots + P_{i_k} y_{k-1} = b - y_k,$$

or, using (5) and (4), we have

$$(6) \quad Ax_k = b - y_k \to b \quad \text{as} \quad k \to \infty, \quad \text{since} \quad y_k \to 0 \quad \text{as} \quad k \to \infty.$$

Thus, $\{x_k\}$ converges to the solution of Eq. (1).

Now consider the system of algebraic linear equations

$$\sum_{i=1}^{n} a_{ji} t_i = b_j \quad (j = 1, 2, \ldots, n).$$

In this case the linear operator A is defined by the matrix $\|a_{ji}\|$. In order to apply the above approximate method it is convenient to take

$$(7) \qquad e_1 = (1, 0, \ldots, 0), \qquad e_2 = (0, 1, 0, \ldots, 0), \ldots, \qquad e_n = (0, \ldots, 0, 1).$$

Then we have $Ae_i = (a_{1i}, a_{2i}, \ldots, a_{ni})$ for $i = 1, 2, \ldots, n$.

The approximate solution is then defined as follows:

$$\frac{1}{\|a_1\|^2}(b, a_1) + \frac{1}{\|a_1\|^2}(y_n, a_1) + \frac{1}{\|a_1\|^2}(y_{2n}, a_1) + \ldots + \frac{1}{\|a_1\|^2}(y_{pn}, a_1) \to t_1 \quad \text{as} \quad p \to \infty,$$

$$\frac{1}{\|a_i\|^2}(y_{i-1}, a_i) + \frac{1}{\|a_i\|^2}(y_{n+i-1}, a_i) + \frac{1}{\|a_i\|^2}(y_{2n+i-1}, a_i) + \ldots$$

$$\ldots + \frac{1}{\|a_i\|^2}(y_{pn+i-1}, a_i) \to t_i \quad \text{as} \quad p \to \infty \quad \text{for} \quad i = 2, 3, \ldots, n,$$

where

$$a_i = (a_{1i}, a_{2i}, ..., a_{ni}), \quad y_1 = b - \frac{1}{\|a_1\|^2}(b, a_1) a_1,$$

$$y_2 = y_1 \frac{1}{\|a_2\|^2}(y_1, a_2) a_2, ..., \quad y_n = y_{n-1} - \frac{1}{\|a_n\|^2}(y_{n-1}, a_n) a_n,$$

$$y_{n+1} = y_n - \frac{1}{\|a_1\|^2}(y_n, a_1) a_1, ... \text{ as in (2).}$$

Remark 1. For the error estimation we have the following recurrent formula obtained from (3):

(8) $$\|y_{k+1}\|^2 = \|y_k\|^2 - \frac{1}{\|a_{i_k}\|^2}(y_k, a_{i_k})^2.$$

In virtue of (6) we put an end to the computations, if $\|y_k\|^2$ is sufficiently small.

Remark 2. If the matrix $\|a_{ji}\|$ is Hermitian and positively defined, then we define in X a new scalar product $[u, v] = (A^{-1}u, v)$, where A is the operator corresponding to this matrix. In this case, the above process coincides with the Gauss-Seidel process. Thus we obtain also a simple proof of the convergence of the Gauss-Seidel iteration process.

2. In this section we shall consider the orthogonal projection from the m-dimensional space X into the subspace $X' \subset X$ spanned by n linearly independent vectors a_i $(i = 1, 2, ..., n < m)$. Denote by P_i the orthogonal projection onto the one-dimensional space generated by the vector a_i.

Theorem 1. *For an arbitrary vector $l \in X$ the sequence $\{y_n\}$ defined by (2) converges to $v = l - Pl$, where Pl is the orthogonal projection of l on X'. If $Pl = \sum_{i=1}^{n} t_i a_i$, then $t_i = \sum_{p=0}^{\infty} \frac{1}{\|a_i\|^2}(y_{pn+i-1}, a_i)$, where $y_0 = l$.*

In fact, consider the orthogonal decomposition of the vector $l = Pl + v$. Denote by $\{y_k'\}$ the sequence (2) in which b is replaced by $l' = Pl$. It is easy to see that $y_k = y_k' + v$ for $k = 1, 2, ...$ It is proved in **1** that the sequence $\{y_k'\}$ converges to the null-vector. Thus $\{y_k\}$ converges to v.

Remark 3. We use formula (8) to find the approximate value of $\|v\|^2 = \lim_{k \to \infty} \|y_k\|^2$ and put an end to computations if $(l, y_k) - \|y_k\|^2$ is sufficiently small, since $(l, y_k) - \|y_k\|^2 = (l - y_k, y_k) \to 0$ as $k \to \infty$.

The orthogonal projection $Pl = \sum_{i=1}^{n} t_i a_i$ is defined by equations

(9) $$\sum_{i=1}^{n} t_i(a_i, a_k) = (l, a_k) \quad \text{for} \quad k = 1, 2, ..., n.$$

THEOREM 2. *The iterative process for finding the orthogonal projection Pl, which is defined by Theorem 1, coincides with the Gauss-Seidel process applied to system* (9).

In fact, let us define the sequence $\{y_k^*\}$ as in (2) under the scalar product $[u, v] = (A^{-1}u, v)$, where A is the operator corresponding to the matrix $\|a_{ki}\|$ for $a_{ki} = (a_i, a_k)$. We have $Ae_i = (a_{1i}, a_{2i}, ..., a_{ni})$ for $i = 1, 2, ..., n$, where e_i is defined by (7). Put

$$l^* = \sum_{k=1}^{n} (l, a_k) e_k, \quad y_1^* = l^* - \frac{[l^*, Ae_1]}{[Ae_1, Ae_1]} Ae_1, \quad y_2^* = y_1^* - \frac{[y_1^*, Ae_2]}{[Ae_2, Ae_2]} Ae_2, ...$$

Since $[y_k^*, Ae_i] = (y_k^*, e_i)$ and $[Ae_k, Ae_k] = a_{kk}$, we shall show by induction that $(y_k, a_i) = (y_k^*, e_i)$. We have $(l, a_i) = (l^*, e_i)$ for $i = 1, 2, ..., n$. Suppose that $(y_k, a_i) = (y_k^*, e_i)$ for $i = 1, 2, ..., n$. Then $(y_{k+1}, a_i) = \left(y_k - \frac{(y_k, a_{j_k})}{\|a_{j_k}\|^2} a_{j_k}, a_i\right) =$

$= (y_k, a_i) - \frac{(y_k, a_{j_k})}{(a_{j_k}, a_{j_k})} (a_{j_k}, a_i) = (y_k^*, e_i) - \frac{(y_k^*, e_{j_k})}{(a_{j_k}, a_{j_k})} (Ae_{j_k}, e_i) = (y_{k+1}^*, e_i)$. The application of Remark 2 completes the proof.

COROLLARY. *The iterative process defined in* **1** *for Eq.* (1) *coincides with the Gauss-Seidel process for equation $A^*Ax = A^*b$.*

In fact, the last equation can be written in the form (9), where $a_i = Ae_i$.

Remark 4. Let us assume that $t_i^0 = 0$ for $i = 1, 2, ..., n$ and t_i^k ($i = 1, 2, ..., n$) is defined by the Gauss-Seidel process applied to system (9). Then we have by Theorem 2

(10) $$y_{nk} = l - \sum_{i=1}^{n} t_i^k a_l.$$

The approximate value of $\|v\|^2$ is in this case defined by the formula

(11) $$\|y_{np}\|^2 = \|l\|^2 - \sum_{k=1}^{p} \sum_{i=1}^{n} (t_i^k - t_i^{k-1})^2 \|a_i\|^2 \to \|v\|^2, \quad \text{as} \quad p \to \infty.$$

It follows from (10) that $\|y_{np} - v\|^2 = \|y_{np}\|^2 - 2\|v\|^2 + \|v\|^2 = \|y_{np}\|^2 - \|v\|^2$.

For the error estimate we can use system (9) directly, by comparing the right-hand sides after substitution of the approximate values of t_i.

The criterion given in Remark 3 is here expressed in the form

$$\sum_{k=1}^{p} \sum_{i=1}^{n} (t_i^k - t_i^{k-1})^2 \|a_i\|^2 - \sum_{i=1}^{n} t_i^k(l, a_i) \to 0 \quad \text{as} \quad p \to \infty.$$

This results from (10) and (11) *).

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*) When the article was finished the author found in [1] the idea, without proof, of the method given in **1** of this paper. This method is also described (in another form) in [3] as presented by A. Svoboda. As remarked in [1], this method was communicated to the author of [1] by de la Garza, whose paper published in Oak Ridge, *K*-25 Plant. Report K-731, is not available so that it is not even registered in *Mathematical Reviews*. However, the results of **2** of the present paper are not contained in the above references. These results are an essential generalisation of **1** and important applications of them will be given elsewhere.

An Approximation Process for the Gaussian Least Squares Principle in the Error Theory

by

M. ALTMAN

Presented by A. MOSTOWSKI on January 30, 1957

In paper [1] is given an approximate method for the solution of linear algebraic equations. It appears that this approximation process has an interesting property. Using this property we obtain an approximate method for the construction of the orthogonal projection on the finite-dimensional subspace.

In the present paper we have applied this method to the Gaussian least squares principle in the error theory. The problem is stated as follows.

Given the following linear system of error equations

$$(1) \qquad v_k = \sum_{j=i}^{m} a_{kj} \dot{x}_j - l_k \quad (k = 1, 2, ..., n; \ n > m),$$

we aim to find the unknown x_j $(j = 1, 2, ..., m)$ such that the minimum is reached for the sum of squares of v_k, i. e.,

$$(2) \qquad \sum_{k=1}^{n} v_k^2 = \text{Min}.$$

The classical direct method of solving this very important problem consists in a reduction to normal equations and in the application of the Gaussian algorithmus to these equations. This method is very convenient if the number of unknowns is not too great. However, there are in practice many very important cases in which the number of unknowns is very great. Therefore, it will be very convenient to have for such cases a direct approximate method, i. e., without reduction to normal equations. Such a method is here suggested.

For this purpose consider the linear n-dimensional Euclidean space E_n with scalar product (a,b) for $a,b \, \epsilon \, E_n$. Denote by a_j $(j=1,2,...,m)$ the columns of the matrix $\|a_{jk}\|$ and assume that the vectors a_j are linearly independent. Denote also by E_m the subspace spanned by the vectors a_j $(j=1,2,...,m)$, $E_m \subset E_n$. The letter l will stand for the vector with co-ordinates l_k $(k=1,2,...,n)$ and v denotes the vector with co-ordinates v_k $(k=1,2,...,n)$.

Then we can write Eq. (1) in the form

$$v = \sum_{j=1}^{m} x_j a_j - l.$$

Condition (2) means that the vector v should be of the least length. But this is the case if $l - v$ is the orthogonal projection of l on E_m, i. e., $v = l - Pl$, where P denotes the orthogonal projection on E_m. Denote by P_i the orthogonal projection on the one-dimensional space generated by the vector a_i for $i=1,2,...,m$. We shall construct an infinite sequence of vectors y_k as follows:

$$y_1 = l - P_1 l, \quad y_2 = y_1 - P_2 y_1, ..., y_m = y_{m-1} - P_m y_{m-1},$$

(3) $\qquad y_{m+1} = y_m - P_1 y_m, \quad y_{m+2} = y_{m+1} - P_2 y_{m+1},$

$$y_{2m+1} = y_{2m} - P_1 y_{2m}, ...$$

The sequence $\{y_k\}$ defined by (3) converges to $v = l - Pl$, where Pl is the orthogonal projection of l on E_m (see [1], Theorem 1).

Now we are in a position to define the above mentioned approximation process. Put $u_1 = (1,0,0,...,0)$, $u_2 = (0,1,0,...,0)$,..., $u_m = (0,...,0,1,1,0,...,0)$, where $u_i \, \epsilon \, E_n$ for $i=1,2,...,m$ and

$$b_1 = \frac{1}{\|a_1\|^2}(l, a_1) u_1, \quad b_2 = \frac{1}{\|a_2\|^2}(y_1, a_2) u_2,..., \quad b_k = \frac{1}{\|a_{i_k}\|^2}(y_{k-1}, a_{i_k}) u_{i_k},$$

i. e., the vector b_k is obtained by replacing the corresponding vector a_{i_k} by u_{i_k} in the orthogonal projection

$$P_{i_k} y_{k-1} = \frac{(y_{k-1}, a_{i_k})}{\|a_{i_k}\|^2} a_{i_k}, \quad \text{where } y_k \text{ is defined by (3).}$$

Thus, we get the following

THEOREM. *The sequence* $\{w_k\}$, *where* $w_k = b_1 + b_2 + ... + b_k$, *converges to the vector* $w = \sum_{j=1}^{m} x_j u_j$ *and* x_j $(j=1,2,...,m)$ *is the solution of the system* (1) *with condition* (2).

For the proof it is sufficient to note that replacing in w_k the vectors u_i by a_i we obtain

$$(4) \qquad P_1 l + P_2 y_1 + \ldots + P_{i_k} y_{k-1} = l - y_k \xrightarrow[k \to \infty]{} l - (l - Pl) = Pl = \sum_{j=1}^{m} x_j a_j.$$

Hence, applying the corresponding linear transformation to the first sum we obtain $w_k \xrightarrow[k \to \infty]{} w = \sum_{j=1}^{m} x_j u_j$.

Remark 1. For the approximate computation of the value $\sum_{i=1}^{n} v_i^2 = \text{Min.}$ it is convenient to use the following recurrent formula:

$$\|y_{k+1}\|^2 = \|y_k\|^2 - \frac{(y_k, a_{i_k})^2}{\|a_{i_k}\|^2} \qquad (1 \leqslant i_k \leqslant m),$$

since this value is a limit of the monotonously decreasing sequence $\{\|y_k\|^2\}$.

Remark 2. To compute the approximate solution we use the following formulae:

$$\frac{1}{\|a_1\|^2}(l, a_1) + \frac{1}{\|a_1\|^2}(y_m, a_1) + \frac{1}{\|a_1\|^2}(y_{2m}, a_1) + \ldots + \frac{1}{\|a_1\|^2}(y_{pm}, a_1) \to x_1 \quad \text{as} \quad p \to \infty,$$

$$\frac{1}{\|a_i\|^2}(y_{i-1}, a_1) + \frac{1}{\|a_i\|^2}(y_{m+i-1}, a_i) + \frac{1}{\|a_i\|}(y_{2m+i-1} a_i) + \ldots +$$

$$+ \frac{1}{\|a_i\|^2}(y_{pm+i-1}, a_i) \to x_i \quad \text{as} \quad p \to \infty \quad \text{for} \quad i = 2, 3, \ldots, m,$$

where $a_i = (a_{1i}, a_{2i}, \ldots, a_{ni})$,

$$y_1 = l - \frac{1}{\|a_1\|^2}(l, a_1) a_1, \quad y_2 = y_1 - \frac{1}{\|a_2\|^2}(y_1, a_2) a_2, \ldots,$$

$$y_m = y_{m-1} - \frac{1}{\|a_m\|^2}(y_{m-1}, a_m) a_m, \, y_{m+1} = y_m - (y_m, a_1) a_1, \ldots$$

as in (3).

Remark 3. For the sake of accuracy of the approximate solution we apply in practice the following criterion, instead of the one expressed by the difference of the vector length:

$$\text{since} \quad (l, y_k) - \|y_k\|^2 = (l - y_k, y_k) \to 0 \quad \text{as} \quad k \to \infty,$$

we put an end to computations if $(l, y_k) - \|y_k\|^2$ is sufficiently small.

Remark 4. We can also obtain another criterion, different from that given in Remark 3. Writing (1) and (4) in the matrix form we have

$$(5) \qquad\qquad l = Aw - v \quad \text{and} \quad l = Aw_k + y_k,$$

where A denotes the matrix $\|a_{ij}\|$.

It follows from the Gaussian normal equations and from (5) and (4) that

$$A^*l = A^*Aw = A^*Aw - A^*v \quad \text{and} \quad A^*l = A^*Aw_k + A^*y_k.$$

Hence, $A^*v = 0$ and $A^*y_k \to 0$ as $k \to \infty$.

Thus, we have $\|A^*A(w_k - w)\|^2 = \|A^*y_k\|^2$, and we obtain by [1] (Remark 4):

$$\|y_k\|^2 - \|v\|^2 = \|y_k + v\|^2 = \|A(w_k - w)\|^2 \leqslant \|A\|^2 \|w_k - w\|^2 \leqslant \|A\|^2 \|(A^*A)^{-1}\|^2 \|A^*y_k\|^2.$$

Remark 5. If we apply the Gauss-Seidel process to the system of normal equations for the solution of (1) under condition (2), then we can use the result of [1], (Remark 4) to obtain some reckoning economy.

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On a Class of B_0-Spaces

by

C. BESSAGA and A. PEŁCZYŃSKI

Presented by S. MAZUR on February 2, 1957

Denote by $\mathfrak{N}$ the class of B_0-spaces *) in which there exists no homogeneous continuous norm. The purpose of the present paper is to give a characterisation of the spaces which belong to the class $\mathfrak{N}$. The selection of this class is useful for the study of properties of Schauder bases in B_0-spaces [1].

Let E be a B_0-space with homogeneous pseudonorms $(|x|_n)$. Let us set

$$(1) \qquad |x|_n^* = \max_{i \leqslant n} |x|_i \qquad (n = 1, 2, ...).$$

THEOREM 1. $E \in \mathfrak{N}$ *if, and only if, none of the pseudonorms (1) is a norm.*

Proof. The necessity of the condition is obvious.

The sufficiency is a simple consequence of the fact that for every homogeneous continuous pseudonorm $|x|$ defined on E there exists a constant $C > 0$ and an index k_0 such that $|x| \leqslant C|x|_{k_0}^*$ ([2] 1.51).

COROLLARY 1. $s \in \mathfrak{N}$ (s *is the B_0-space of all sequences of real numbers* $x = (\xi_n)$ *with pseudonorms* $|x|_n = |\xi_n|$ $(n = 1, 2, ...)$).

More generally, if E is a relatively complete B_0-space [4] which is not a Banach space, then $E \in \mathfrak{N}$.

THEOREM 2. $E \in \mathfrak{N}$ *if, and only if, there exists a B_0-space E_1 and a space X isomorphic to s such that $E = E_1 \times X$.*

Proof. The sufficiency of the condition immediately follows from Collorary 1. The necessity is the consequence of the following lemmas:

LEMMA 1. *If* $E \in \mathfrak{N}$, *then there exists a subspace* $X \subset E$ *which is isomorphic to* s.

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*) For the definition of B_0-spaces and related notions see [2] and [3].

LEMMA 2. *If a subspace $X \subset E$ is isomorphic to s, then X is a projection of E.*

Proof of Lemma 1. It follows from the hypothesis of the Lemma that there exists an increasing sequence (k_n) of indices and a sequence (e_n) of elements of the space such that

(2) $$|e_n|_j = \begin{cases} 0 & \text{for} \quad j < k_n \\ 1 & \text{for} \quad j = k_n \end{cases} \quad (n = 1, 2, \ldots).$$

An inductive definition of the sequences (k_n) may here be omitted.

It follows from (2) that if $(t_n) \in s$, then the series $\sum_{n=1}^{\infty} t_n e_n$ is convergent; and if $\sum_{n=1}^{\infty} t_n e_n = \sum_{n=1}^{\infty} t'_n e_n$, then $(t_n) = (t'_n)$. It follows that the smallest closed linear space containing the elements $e_1, e_2, \ldots$ is isomorphic to s.

Proof of Lemma 2. Let A be an isomorphism of X onto s, A^* — the conjugate operation to A. Setting $\varphi_i((\xi_n)) = \xi_i$ $(i = 1, 2, \ldots)$ for $(\xi_n) \in s$ we have $\varphi_i \in s^*$, (the symbol Y^* denotes the space conjugate to Y). Let $\bar{\psi}_i \in E^*$ be an extension of the functional $\psi_i = A^* \varphi_i$ $(i = 1, 2, \ldots)$ to a functional defined on E. The operation $U(x) = A^{-1}(\bar{\psi}_i(x))$ is a projection of E onto X.

In the sequel we shall give an interior characterisation of the space s.

Let $E(|x|_k)$ denote the quotient space $E/\{x \in E : |x|_k = 0\}$ with the norm induced by the pseudonorm $|x|_k$.

THEOREM 3. *An infinitely dimensional B_0-space X is isomorphic to s if, and only if, the dimension of each space $X(|x|_k)$ $(k = 1, 2, \ldots)$ is finite.*

Proof. The sufficiency of the condition follows immediately from [2] 1.51 (see the proof of Theorem 1).

Necessity. If the spaces $X(|x|_k)$ have finite dimensions, then so do the spaces $X(|x|_k^*)$. Let $r_k = \dim X(|x|_k^*)$ $(k = 1, 2, \ldots)$. It may be supposed that $1 \leqslant r_1 < r_2 < \ldots$ One may easily define by induction a sequence (e_n) of elements of X such that:

1° the elements $e_1, e_2, \ldots, e_{r_k}$ are linearly independent with respect to the pseudonorm $|x|_k^*$ for $k = 1, 2, \ldots$, i. e.,

(3) $|t_1 e_1 + t_2 e_2 + \ldots + t_{r_k} e_{r_k}|_k^* = 0$ implies $t_1 = t_2 = \ldots = t_{r_k} = 0$

for arbitrary real numbers $t_1, t_2, \ldots, t_{r_k}$.

2° $|e_n|_k^* = 0$ for $n \leqslant r_{k-1}$ $(k = 2, 3, \ldots)$.

It may be easily shown that:

(a) for every $(t_n) \in s$ the series $\sum_{n=1}^{\infty} t_n e_n$ is convergent;

(b) if $x \in X$, then there exists one, and only one, $(t_n) \in s$ such that
$$x = \sum_{n=1}^{\infty} t_n e_n.$$

Setting $U(x) = (t_n)$ we obtain the required isomorphism of X onto s.

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An Extension of the Krein-Milman-Rutman Theorem Concerning Bases to the Case of B_0-Spaces

by

C. BESSAGA and A. PEŁCZYŃSKI

Presented by S. MAZUR on February 2, 1957

Krein, Milman and Rutman [2] have proved:

If X is a Banach space having a basis, then a basis of the space X may be chosen from an arbitrary dense subset of X.

We shall prove that the following theorems hold true in the case of B_0-spaces *).

THEOREM 1. *If E is a B_0-space having a basis, then a basis of E may be chosen from an arbitrary dense subset of E if, and only if, $E \in \mathfrak{N}$, i. e., according to the definition given in* [1] *there exists a homogeneous continuous norm defined on E.*

THEOREM 2. *The space s is up to an isomorphism the unique B_0-space of the class $\mathfrak{N}$ containing a basis (for the whole space) in every linear dense subset.*

I. Notations. If Z is a set of elements of a B_0-space, then $R(Z)$ denotes the smallest linear subset of the space containing Z; $\bar{Z}$ denotes the closure of Z.

$E_1 \oplus E_2$ denotes the direct sum of spaces E_1 and E_2.

The symbol E is reserved for B_0-spaces, $\|x\|$ denotes the norm of this space and $(|x|_k)$ — the system of homogeneous pseudonorms equivalent to the norm.

II. The proof of Theorem 1 is based on several lemmas.

LEMMA 1. *Let $(e_n) \subset E$, $\overline{R(\{e_n\})} = E$. The sequence (e_n) is a basis of E if, and only if, there exists a norm $\||x\||$ defined on E equivalent to $\|x\|$, such that*

$$(1) \qquad \||t_p e_p + t_{p+1} e_{p+1} + \ldots + t_q e_q\|| \leqslant \||t_1 e_1 + t_2 e_2 + \ldots + t_q e_q\||$$

for arbitrary positive integers p and q $(p \leqslant q)$ and arbitrary reals $t_1, t_2, \ldots, t_q$.

---

*) For the definition of B_0-spaces and related notions see [3] and [4].

The proof of this lemma is given in [5].

Let us denote

$$(2) \qquad |x|_k^* = \max_{i \leqslant k} |x|_i \quad (k = 1, 2, ...).$$

Suppose that (e_n) is a basis of E and let

$$(3) \qquad x = \sum_{i=1}^{\infty} \varphi_i(x) e_i$$

for every $x \in E$.

It is easy to deduce from Lemma 1 the following one.

LEMMA 2. *If (e_n) is a basis of E, then the formulae*

$$(4) \qquad \|x\|_k = \sup_m \left| \sum_{i=m}^{\infty} \varphi_i(x) e_i \right|_k^* \quad (k = 1, 2, ...)$$

define a system of homogeneous pseudonorms which is equivalent to the system $(|x|_k)$.

LEMMA 3. *If (e_n) is a basis of a Banach space X, the functionals φ_n $(n = 1, 2, ...)$ are defined by (3) and a sequence $(f_n) \subset X$ satisfies the condition*

$$\sum_{n=1}^{\infty} |f_n - e_n| \, |\varphi_n| < 1;$$

then (f_n) is a basis of X.

Lemma 3 is proved in [2].

We shall now show that the condition of Theorem 1 is sufficient. Let $E \in \mathfrak{N}$, and let (e_n) be a basis of E. Without the loss of generality, we may suppose that each pseudonorm $|x|_i$ $(i = 1, 2, ...)$ is a norm and

$$(5) \qquad |e_i|_1^* = 1 \quad (i = 1, 2, ...).$$

Notice that from (2) and (4) there follows

$$(6) \qquad \|x\|_1 \leqslant \|x\|_2 \leqslant ...,$$

but from (4) and (5) there follows

$$(7) \qquad |\varphi_i(x)| \leqslant 2 \cdot \|x\|_k \quad i, k = 1, 2, ...$$

Let $\breve{E}_k$ denote the completion of the space E considered with the one norm $\|x\|_k$. This completion is clearly a Banach space. According to Lemma 1 and formula (4),

(*) the sequence (e_n) is a basis of each of the spaces $\breve{E}_k$.

Let Z be a dense subset of E. Choose a sequence $(f_n) \subset Z$, such that

$$(8) \qquad 2 \cdot \|e_n - f_n\|_n \leqslant 2^{-n-1}.$$

From (6), (7), and Lemma 3 we infer that

(**) (f_n) is a basis of the space $\breve{E}_1$.

(***) $(f_k, f_{k+1}, ...)$ is a basis of the space $\breve{E}_k^k$. ($\breve{E}_k^i$ $(i, k = 1, 2, ...)$ denotes the closure of the set $R(\{e_i, e_{i+1}, ...\})$ in relation to the space $\breve{E}_k$.

We shall prove that

$$(9) \qquad \breve{E}_k = R(\{f_1, f_2, ..., f_{k-1}\}) \oplus \breve{E}_k^k.$$

The dimension of the subspace $R(\{f_1, f_2, ..., f_{k-1}\})$ is by (**) equal to $k-1$. The defect of the subspace $\breve{E}_k^k$ with respect to E_k is equal to $k-1$, because by (*) $R(\{e_1, e_2, ..., e_{k-1}\}) \oplus \breve{E}_k^k = E$.

If

$$(10) \qquad x = t_1 f_1 + t_2 f_2 + ... + t_{k-1} f_{k-1} \,\epsilon\, R(\{f_1, f_2, ..., f_{k-1}\}) \oplus \breve{E}_k^k,$$

then by (**) there exists a sequence $(t_k, t_{k+1}, ...)$ of real numbers such that

$$\lim_{n \to \infty} \left\| t_1 f_1 + t_2 f_2 + ... + t_{k-1} f_{k-1} - \sum_{i=k}^{k+n} t_i f_i \right\|_k = 0.$$

Hence by (6)

$$\lim_{n \to \infty} \left\| t_1 f_1 + t_2 f_2 + ... + t_{k-1} f_{k-1} - \sum_{i=k}^{\epsilon+n} t_i f_i \right\|_1 = 0,$$

whence by (**) $t_1 = t_2 = ... = 0$, i. e., $x = 0$. Formula (9) is thus proved.

From (9), (**), and (***) it follows that (f_n) is a basis of each of the spaces $\breve{E}_k$ $(k = 1, 2, ...)$; from (7) we infer that (f_n) is a basis of the B_0-space E.

We shall further need the following lemmas:

LEMMA 4. *If (e_k) is a basis of E and $E \,\epsilon\, \mathfrak{N}$, then there exists a subsequence (e_{n_k}), such that the series $\sum_{k=1}^{\infty} t_k e_{n_k}$ is convergent for an arbitrary sequence (t_k) of real numbers.*

Proof. According to Lemma 2, the pseudonorms (4) are continuous, hence none of them is a norm (by hypothesis that $E \,\epsilon\, \mathfrak{N}$). From the formulae (4) it follows that for every positive integer k there exists an index j_k such that $|e_{j_k}|_k^* = 0$. The sequence (j_k) is not bounded, otherwise we would have $\sup_{i \leqslant k} |e_j|_i = 0$ for a fixed j and for infinitely many k, i. e., it would be $e_j = 0$, which is impossible for an element of a basis. Let $(n_k) = (j_{p_k})$ $(k = 1, 2, ...)$, be an increasing subsequence of the sequence (j_k).

We have $|e_{n_k}|^*_{p_k} = 0$ and hence by (2) $|e_{n_{k'}}|_k = 0$ for $k' > k$, $k = 1, 2, ...$ This implies the following Lemma.

LEMMA 5. *If $E \in \mathfrak{R}$ and $\|x\|$ is an arbitrary homogeneous continuous pseudonorm defined on E, then the set $Z = \{x \in E : |x| \neq 0\}$ contains no basis of E.*

In fact, let (z_k) be an arbitrary sequence of elements of Z. The series $\sum_{k=1}^{\infty} \frac{1}{|z_{n_k}|} z_{n_k}$ is clearly divergent for every subsequence (z_{n_k}) of (z_k). Hence, by Lemma 4 no sequence of elements of Z is a basis of E.

We shall now show that the condition of Theorem 1 is necessary. Supposing that the homogeneous pseudonorm $|x|_1$ is not identically equal to 0, we obtain that the set $Z = \{x \in E : |x|_1 \neq 0\}$ is dense in E; according to Lemma 4, Z contains no basis of the space E.

III. Proof of Theorem 2. Obviously, every dense linear subset of the space s contains a sequence (e_n), $e_n = (\eta_k^n)$ $(n = 1, 2, ...)$, such that $\eta_n^n \neq 0$, $\eta_k^n = 0$ for $n > k$ $(k = 1, 2, ...)$. The sequence (e_n) is a basis of s.

Let E be a space belonging to $\mathfrak{R}$ which is not isomorphic to s. We shall consider the only essential case of separable E. According to [1] (Theorem 3) there exists a continuous homogeneous pseudonorm $|x|$ defined on E such that the dimension of the space $E(|x|)$ [1] is infinite. Let (y_n) be a sequence of elements linearly independent with respect to the pseudonorm $|x|$ [1], (3). We may suppose that

$$\|y_n\| \to 0. \tag{11}$$

Let $\overline{\{x'_n\}} = E$. It is easy to define by induction a sequence (x_n) of elements and an increasing sequence (k_n) of indices such that the following conditions are satisfied:

$$x_n = \begin{cases} x'_n & \text{if } x_1, x_2, ..., x_{n-1}, x'_n \text{ are linearly independent} \\ & \quad \text{with respect to } |x|, \\ x_n + y_{k_n} & \text{if } x_1, x_2, ..., x_{n-1}, x'_n \text{ are linearly dependent} \\ & \quad \text{with respect to } |x|, \end{cases} \tag{12}$$

$$x_1, x_2, ..., x_{n-1}, y_{k_n} \quad \begin{array}{l} \text{are linearly independent with} \\ \text{respect to the pseudonorm } |x|. \end{array} \tag{13}$$

Since $\varrho(x'_n, x_n) \leqslant |y_{k_n}| \to 0$, we obtain $\overline{\{x_n\}} = E$ and $R(\overline{\{x_n\}}) = E$. From (12) and (13) it follows that the elements of the sequence (x_n) are linearly independent with respect to the pseudonorm $|x|$. Hence $R(\{x_n\}) \subset Z + \{0\}$ and, according to Lemma 5, the linear set $R(\{x_n\})$ contains no basis of E.

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On a Certain Variation Problem in P-Geometry and Its Relations to Physical Problems

by

W. SŁOWIKOWSKI

Presented by K. BORSUK on February 20, 1957

1. Introduction. The notion of a P-vector field has been introduced in paper [1]. It follows from [1] that a P-vector field induces a metric and affine connexion. The differential geometry with such a metric and affine connexion will be named P-geometry induced by the given P-vector field. The correspondence between skew-symmetric real valued tensors and P-scalars has been given in [1] too. Every skew symmetric tensor of second rank F_{ij} has been represented by the P-scalar $\mathbf{f} = F_{ij}\mathbf{g}^{ij}$.

In the present paper the integral

$$(1) \qquad I(\mathbf{a}) = \int_{\Omega} \overset{\smile}{\mathbf{g}} \{(\mathbf{f}, \mathbf{f}) - \lambda(\mathbf{a}, \mathbf{a}) - \mu(\mathbf{a}, \mathbf{i})\} \, dv$$

is considered, where Ω is a fixed four dimensional domain, $\mathbf{i} = \bar{\mathbf{i}}$ a fixed P-scalar, $\mathbf{a} = \bar{\mathbf{a}} = A_i\mathbf{g}^i$ and

$$(2) \qquad F_{ij} = \partial_{[i}A_{j]} - S^k_{ij}A_k - S_{[i}A_{j]}, \quad \text{where} \quad S_i \overset{\text{def}}{=} S^k_{ki}.$$

In particular, the extremals of (1) satisfying the condition

$$(3) \qquad (\nabla^l - S^l)A_l = 0$$

will be found. The form of tensor (2) is chosen in such a way that we obtain the equations of extremals only by application of the operator $\mathbf{D} - \mathbf{s}$, where

$$\mathbf{s} = S_i\mathbf{g}^i.$$

Hence the vector S_i plays such an important geometrical role. There are indications that the vector S_i may be physically interpreted as the potential of electromagnetic field induced by the P-vector field $\mathbf{g}_i$ together with the tensor of gravitation g_{ij}.

2. The equations of extremals of (1). Let us consider the functional $I(a)$. We have the following

THEOREM 1. *A solution of equations*

(4)
$$\frac{1}{2}(\mathbf{D} - \mathbf{S})\mathbf{a}^* = \mathbf{f},$$
$$\frac{1}{2}(\mathbf{D} - \mathbf{S})^* \mathbf{f} = \lambda \mathbf{a}^* + \frac{1}{2}\mu \mathbf{i}^*$$

gives the extremals of (1) *(real and imaginary parts together) satisfying the condition* (3).

3. The vector form of the invariant (f, f) and of Eq. (4).

THEOREM 2. *Let* $\mathbf{f} \in \overset{(2)}{\mathfrak{B}}$ *and* $(F_{ij}) \in \overset{(2)}{\mathfrak{U}}$ [1], *and let* $\mathbf{f} = \mathbf{g}^{ij} F_{ij}$.

Then

$$(\mathbf{f},\,\mathbf{f}) = \frac{1}{2} F^{ij} F_{ij} + \frac{1}{4} F_{ij} F_{kl} \hat{\mathbf{g}} \varepsilon^{ijkl}.$$

Theorem 4. of [1] yields the correspondence between invariant and covariant differentiation. Now, we present analogous correspondence for the following more general scalar-operator $\mathbf{D} - \mathbf{p}$ and vector-operator $V_i - P_i$; where $\mathbf{p} = P_i \mathbf{g}^i$.

THEOREM 3. *Let* $\mathbf{x} \in \overset{(n)}{\mathfrak{B}}$ *and* $(X_{i_1 i_2 \ldots i_n}) \in \overset{(n)}{\mathfrak{U}}$ [1] *correspond to each other as follows*

$$\mathbf{x} = \mathbf{g}^{i_1 i_2 \ldots i_n} X_{i_1 i_2 \ldots i_n}.$$

Then

$$(\mathbf{D} - \mathbf{p})^* \mathbf{x} = (n+1) \bar{\mathbf{g}}^{i_0 i_1 \ldots i_n} (V_{[i_0} - P_{i_0}) X_{i_1 i_2 \ldots i_n]} +$$
$$+ \bar{\mathbf{g}}^{i_2 \ldots i_n} (V^{i_1} - P^{i_1}) X_{i_1 i_2 \ldots i_n},$$

where $\mathbf{p} = P_i \mathbf{g}^i$.

Transforming Eq. (4) according to Theorem 3 we obtain

(5)
$$F_{ij} = (V_{[i} - S_i) A_{j]}, \quad (V^i - S^i) A_i = 0, \quad (V_{[i} - S_i) F_{jk]} = 0,$$
$$(V_i - S_i) F_{ij} = 2\lambda A_j + \mu I_j,$$

where $\mathbf{i} = J_j \mathbf{g}^j$.

It is easy to see that Eqs. (4) are similar to the non-homogeneous Dirac equations, where $\mathbf{s}$ is the electromagnetic potential vector. Eqs. (5) correspond to equations of Maxwell and Proca.

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On a Certain Subclass of (DF) Linear Locally Convex Spaces

by

W. SŁOWIKOWSKI

Presented by W. ORLICZ on February 15, 1957

In a paper by Grothendieck [1] the class of (**DF**) spaces has been defined as follows: the locally convex linear space X is named a (**DF**) space if and only if, it satisfies the conditions:

α) there is the sequence (B_n) of bounded subsets of X such that every bounded subset of X is contained in at least one B_n;

β) every bounded subset A of the strong dual X' of the space X which is a union of a sequence of equicontinuous subsets of X', is itself an equicontinuous subset of X'.

The two conditions together are characteristic for the class of spaces containing dual spaces of metrisable locally convex spaces and dual spaces of which are metrisable spaces. Thus the following assertions are true:

1. *The strong dual of a locally convex metrisable space is* (**DF**) *space.*

2. *The strong dual of a* (**DF**) *space is a locally convex metrisable space.*

In [2] the notion of the *strongest dual of locally convex linear space* has been introduced. The question arose whether the analogous class of spaces, as regards the strongest duality, may be defined.

The answer is positive and the class of spaces obtained in such a way is smaller than the class of (**DF**) spaces. It may be characterised as follows.

D e f i n i t i o n. The linear locally convex space X is named (**DB$_0$**) *space* if X is bornological space and if there is a sequence (X_n) of Banach spaces such that:

α) X_n are linear subsets of X; the identical imbedding of X_n into X is continuous;

β) every bounded subset of X is bounded in at least one X_n.

We have the following:

THEOREM 1. *Every* (**DB$_0$**) *space is* (**DF**) (*t*)-*space*.

2. *The strongest dual and strong dual of a* (**DB$_0$**) *space are identical and both are* (**B$_0$**) *spaces* (i. e. linear locally convex complete metrisable space [3]).

3. *The strongest dual of metrisable locally convex space is a* (**DB$_0$**) *space*.

4. The class of (**B$_0$**) spaces [3] and the class of (**DB$_0$**) spaces belong to the same class **K** of linear locally convex spaces with the *Banach Inversion Property* *). (We say that a class **K** of linear locally convex spaces has the *Banach Inversion Property*, if every continuous one-to-one linear mapping of a space $X \in \mathbf{K}$ onto the space $Y \in \mathbf{K}$ is bicontinuous [4]).

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*) This class of spaces will be discussed in a separate paper.

On Spaces of Functions of Finite Generalised Variation

by

J. MUSIELAK and W. ORLICZ

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1. Let $M(u)$ denote a continuous and non-decreasing function défined for $u \geqslant 0$ with $M(0) = 0$, $M(u) > 0$ for $u > 0$. We shall use in sequel the following conditions

(0) there exist $a > 0$ and $L > 0$ such that $M(u) \leqslant Lu$ for $0 < u < a$,

(o) $M(u)/u \to 0$ for $u \to 0$,

(Δ_2) there exist $a > 0$ and $\varkappa > 0$ such that $M(2u) \leqslant \varkappa M(u)$ for $0 < u < a$,

(c) the function $M(u)$ is a convex one.

We shall sometimes use function $N(u)$ satisfying the same conditions as $M(u)$.

1.1. Let $x(t)$ be a real or complex-valued function defined for $a \leqslant t \leqslant b$, and let Π denote an arbitrary partition $a = t_0 < t_1 < \ldots < t_m = b$ of the interval $\langle a, b \rangle$. We call

$$V_M(x) = \sup_\Pi \sum_{i=1}^m M[|x(t_i) - x(t_{i-1})|]$$

the *total M-variation* of the function $x(t)$ in $\langle a, b \rangle$ (see [6], p. 582). We denote by V_M the class of all functions $x = x(t)$, $x(a) = 0$, with $V_M(x) < \infty$ and by V_M^* the class of all functions $x = x(t)$ such that for a $k > 0$ (depending on x), $kx \in V_M$.

1.11. It may be proved (analogically to [1], p. 5, Theorem 1a) that $V_M \subset V_N$, if and only if, there exist $a > 0$ and $b > 0$ such that $N(u) \leqslant bM(u)$ for $0 < u < a$.

Hence we obtain the following theorem.

1.12. *The class V_M is linear, if and only if, (Δ_2) is satisfied (for the proof compare [5], p. 208, Theorem 1). If* (c) *is satisfied, then the class V_M^* is linear; if we suppose (Δ_2), $V_M^* = V_M$.*

1.2. In the class V_M^* the convergence in variation may be introduced. We say that the sequence $x_n = x_n(t)$ is convergent in variation to $x = x(t)$, if there exists a $k > 0$ (not depending on n) such that $V_M[k(x_n - x)] \to 0$ for $n \to \infty$.

1.21. Assuming (Δ_2), a sequence $x_n(t)$ is convergent in variation to $x(t)$, if and only if, $V_M(x_n - x) \to 0$ for $n \to \infty$. Moreover, if we suppose (Δ_2), the space V_M is a complete (i. e., Cauchy-condition implies convergence) and non-separable $\mathcal{L}^*$-space with respect to convergence in variation (for terminology, see [2], pp. 83 and 88).

1.3. The following generalised Helly extracting-theorem holds

If $x_n \in V_M^*$ and $V_M(kx_n) \leqslant K$ for $n = 1, 2, \ldots$ and for certain $k > 0$ and $K > 0$, then there exists a subsequence of the sequence $x_n(t)$ convergent to a function $x = x(t)$ of the class V_M^* for every $t \in \langle a, b \rangle$.

This theorem holds for arbitrary $M(u)$; its proof does not require any of the conditions (0) (o), (Δ_2), (c).

1.4. Now we introduce classes AC_M and AC_M^* of functions, *absolutely continuous* in a generalised sense. The class AC_M for $M(u) = u^\alpha$ $(a > 1)$ was introduced by E. R. Love in [3], p. 2.

We say that the function $x = x(t)$, where $x(a) = 0$, belongs to AC_M, if for every $\varepsilon > 0$ there exists a $\delta > 0$ such that

$$\sum_{i=1}^{m} M[|x(\beta_i) - x(a_i)|] < \varepsilon,$$

for all finite sets of non-overlapping intervals $(a_i, \beta_i) \subset \langle a, b \rangle$ $(i = 1, 2, \ldots, m)$ such that

$$\sum_{i=1}^{m} M(\beta_i - a_i) < \delta.$$

By AC_M^* we denote the class of all functions $x = x(t)$ such that for a $k > 0$ (depending on x), $kx \in AC_M$.

1.41. If we suppose $M(u)$ to satisfy (0) and (Δ_2), the class AC_M is complete with respect to the convergence in variation. Assumptions (o) and (Δ_2) imply AC_M to be separable w th regard to the convergence in variation and assumptions (o) and (c) imply the same for AC_M^*

1.5. *Let us suppose $M(u)$ to satisfy* (o) *and* (c) *and let $x = x(t)$ be a measurable and periodic function with period $b - a$. Denote $x_h = x \, (t + h)$. Then $x \in AC_M^*$, if and only if, there exists a $k > 0$ (depending on x) such that $V_M[k(x_h - x)] \to 0$ for $h \to 0 +$.*

One can obtain the proof of this theorem by a suitable generalisation of arguments used in [3]. In the proof of necessity of the condition $V_M[k(x_h - x)] \to 0$ the assumption (c) may be replaced by $(\varDelta_2)$. Theorem 1.5 may be also generalised to non-periodic functions.

2. For our further considerations we suppose (c) to be satisfied. We introduce in V_M^* the homogenous norm $\|x\|$ as the least constant $k \geqslant 0$ such that $V_M(x/k) \leqslant 1$. It is easily seen that for $M(u) = u^\alpha$ $(\alpha \geqslant 1)$,

$$\|x\| = \left[\sup_\Pi \sum_{i=1}^m |x(t_i) - x(t_{i-1})|^\alpha \right]^{1/\alpha}.$$

2.1. The class V_M^* with norm $\|x\|$ and the usual definitions of addition and scalar-multiplication of elements is a complete and non-separable Banach space. If we suppose $(\varDelta_2)$ to be satisfied, then AC_M^* is a separable complete subspace of V_M^*.

2.11. The norm-convergence implies in V_M^* convergence in variation to the same limit. When $M(u)$ satisfies $(\varDelta_2)$, norm-convergence and convergence in variation are in V_M^* equivalent.

2.2. Let us suppose $M(u)$ to satisfy (o), (c) and $M(u)/u \to \infty$ for $u \to \infty$. Then there exists a function $N(u)$, called complementary to $M(u)$ and satisfying also (o), (c) and $N(u)/u \to \infty$ for $u \to \infty$ (for definition see, e. g. [1], p. 15, Theorem 4). Now we introduce in V_M^* a second norm $\|x\|^0$ as the upper bound of the set of numbers

$$\sum_{i=1}^m [x(t_i) - x(t_{i-1})] b_i,$$

whenever $a = t_0 < t_1 < \ldots < t_m = b$, $\sum_1^m N(|b_i|) \leqslant 1$ and $m = 1, 2, \ldots$

2.21. Under assumptions of **2.2** the inequalities

$$\|x\| \leqslant \|x\|^0 \leqslant 2\|x\|$$

hold for every $x \, \epsilon \, V_M^*$.

2.3. Functionals $\xi(x) = x(t_0)$ (t_0 fixed) are evidently linear over the Banach space V_M^*. Let $\varXi_0$ be the set of all finite linear combinations η of the form

$$\eta(x) = \sum_{i=1}^m [\xi_i(x) - \xi_{i-1}(x)] b_i$$

with

$$\sum_1^m N(|b_i|) \leqslant 1, \quad \xi_i(x) = x(t_i), \quad a = t_0 < t_1 < \ldots < t_m = b, \quad m = 1, 2, \ldots$$

The set Ξ_0 is under assumptions of **2.2** a fundamental one, that is

$$\|\eta\| < C \quad \text{and} \quad \sup_{\eta \in \Xi_0} |\eta(x)| \geqslant c\|x\|$$

for certain $C > 0$ and $c > 0$.

2.31. It follows from **1.3** and **2.3** that under assumptions of **2.2**, every sequence of elements of V_M^* bounded with respect to the norm contains a subsequence weakly convergent with respect to the fundamental set of linear functionals Ξ_0.

2.32. Weak convergence of a sequence $x_n \in V_M^*$ with respect to the fundamental set Ξ_0 implies under assumptions of **2.2**

$$\|x\| \leqslant \lim_{n \to \infty} \|x_n\| \quad \text{and} \quad \|x\|^0 \leqslant \lim_{n \to \infty} \|x_n\|^0.$$

3. Spaces of functions of finite generalised variation find, as follows from papers of L. C. Young and E. R. Love, interesting applications, e. g., in the theory of Stieltjes integral and in the theory of Fourier series (for bibliographical data, see [3] and [6]). Spaces considered in **2** are connected with the general theory of modular spaces of Nakano [4]. The authors will return, in a further note, to investigations of spaces V_M^*, especially to the representation of linear functionals over certain subspaces of V_M^* in the form of Stieltjes integrals and related problems.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

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Some Remarks on Non-Local Theories

by

J. RZEWUSKI

The necessity to construct a new theory of elementary particles seems to be a well established fact. On the one hand recent experimental results on scattering of electrons on nucleons [1], [2] indicate that the elementary particles possess a finite size. On the other hand it is well known that the conventional local theories are full of inconsistencies. The drastic character of the latter was exhibited particularly clearly by some recent theoretical results concerning the renormalisation procedure [3]—[5]. Finally, an abundance of data concerning the various kinds of new particles remains so far without any theoretical explanation.

There exist so far only two modifications of the conventional quantum theory of local fields. One is the theory of bi-local fields proposed by Yukawa [6] and Markov [7] and developed by Rayski [8]. It provides us with a concrete model of elementary particles and at the same time offers the possibility to explain their mass spectra. The other is the theory of local fields with non-local interaction proposed by Peierls and McManus [11]. It gives account of the finite size of the particle without giving any specific picture of its structure.

Both theories possess serious disadvantages as e. g. the lack of causality and the indeterminate character of the formfactors in the theory of non-local interaction [12]—[17] and the difficulties in introducing interaction in the bi-local theories. It seems however that these disadvantages are not sufficient to discriminate both theories altogether.

In this note we wish to make some comments on non-local as well as on bi-local theories from a general point of view comprising both theories. This point of view enables one to see more clearly the consequences of certain particular models proposed so far. It also brings into the foreground a new problem, namely the hyperbolic eigenvalue problem.

We consider two bi-local scalar fields, one real field $\varphi(x,r)$ and one complex field $\psi(x,r)$. x is a point in Minkowski's space and r a point of

some other space. We may denote the pair of points x and r by ω and the volume element $dx\,dr$ by $d\omega$.

Let us assume that the fields are described by the action functional

$$(1) \qquad W = \int \overset{0}{\mathcal{L}}(\omega)\,d\omega + g \int\int\int \overset{1}{\mathcal{L}}(\omega',\omega'',\omega''')\,d\omega'd\omega''d\omega''',$$

where $\overset{0}{\mathcal{L}}$ is some bilinear function of φ and ψ their derivatives with respect to x and r (up to an arbitrary order) and

$$(2) \qquad \overset{1}{\mathcal{L}}(\omega',\omega'',\omega''') = M(\omega',\omega'',\omega''')\psi^*(\omega')\varphi(\omega'')\psi(\omega'''),$$

where $M(\omega',\omega'',\omega''')$ is some given function of ω',ω'' and ω'''.

The corresponding Lagrange equations may be written in the form

$$(3) \qquad \begin{cases} \left(\dfrac{\partial^2}{\partial x_\mu^2} - \mathrm{M}^2\right)\varphi(\omega) = g\int\int M(\omega',\omega,\omega''')\psi^*(\omega')\psi(\omega''')\,d\omega'd\omega''' \\[2mm] \left(\dfrac{\partial^2}{\partial x_\mu^2} - \varLambda^2\right)\psi(\omega) = g\int\int M(\omega,\omega'',\omega''')\varphi(\omega'')\psi(\omega''')\,d\omega''d\omega'''. \end{cases}$$

Here M^2 and $\varLambda^2$ are uniquely determined by $\overset{0}{\mathcal{L}}$ and may be considered as mass operators corresponding to the fields φ and ψ respectively. M^2 and $\varLambda^2$ will contain in general the variables r and the derivatives with respect to x and r. Dependence on x is excluded by the demand of invariance with respect to translations in Minkowski's space.

Due to the possible occurrence of the derivatives $\partial/\partial x_\mu$ in the mass operators M^2 and $\varLambda^2$ it is convenient to go over into momentum space with respect to the variable x

$$(4) \qquad \begin{cases} \varphi(x,r) = \dfrac{1}{(2\pi)^4}\int \varphi(k,r)e^{ik_\mu x_\mu}dk, \quad \psi(x,r) = \dfrac{1}{(2\pi)^4}\int \psi(k,r)e^{ik_\mu x_\mu}dk, \\[2mm] M(x',r';\,x'',r'';\,x''',r''') = \\[2mm] = \dfrac{1}{(2\pi)^{12}}\int\int\int M(k',r';\,k'',r'';\,k''',r''')\,e^{ik'_\mu x'_\mu + ik''_\mu x''_\mu - ik'''_\mu x'''_\mu}\,dk'dk''dk'''. \end{cases}$$

Denoting the pair k, r by ϱ and the volume element $dk\,dr$ by $d\varrho$ we may write the transformed equations in the form

$$(5) \qquad \begin{cases} (-k_\mu^2 - \mathrm{M}^2)\varphi(\varrho) = \dfrac{g}{(2\pi)^8}\int\int M(\varrho',\varrho,\varrho''')\psi^*(\varrho')\psi(\varrho''')\,d\varrho'd\varrho''', \\[2mm] (-k_\mu^2 - \varLambda^2)\psi(\varrho) = \dfrac{g}{(2\pi)^8}\int\int M(\varrho,\varrho'',\varrho''')\varphi^*(\varrho'')\psi(\varrho''')\,d\varrho''d\varrho'''. \end{cases}$$

M^2 and $\varLambda^2$ appear now as functions of the point r, of the derivatives with respect to r and of the point k. The co-ordinates of the point $k(k_1,k_2,k_3,k_0)$ appear as parameters, whereas the co-ordinates of the

point r (which we shall denote by r_α without special'sing the number of dimensions and the metric of the r-space) and the derivatives $\partial/\partial r_\alpha$ play an essential rôle.

We assume now that the differential operators $\mathbf{M}^2$ and Λ^2 are such that they admit solutions $f_n(k, r) \equiv f_n(\varrho)$ and $p_n(k, r) \equiv p_n(\varrho)$ of the following eigenvalue problems

$$(6) \qquad \mathbf{M}^2\left(ik_\mu, r_\alpha, \frac{\partial}{\partial r_\alpha}\right) f_n(\varrho) = m_n^2 f_n(\varrho); \qquad \Lambda^2\left(ik_\mu, r_\alpha, \frac{\partial}{\partial r_\alpha}\right) p_n(\varrho) = \lambda_n^2 p_n(\varrho),$$

$$(7) \qquad \int f_n^*(\varrho) f_m(\varrho) dr = \delta_{nm}; \qquad \int p_n^*(\varrho) p_m(\varrho) dr = \delta_{nm}.$$

Eqs. (6) and (7) are supposed to hold for all values of the parameters k. The eigenvalues m_n^2 and λ_n^2 are supposed to be independent of k. The latter assumption means simply that the rest mass of a particle is independent of its momentum.

By virtue of (6) and (7) we may expand the scalars $\varphi(\varrho)$ and $\psi(\varrho)$ in series of the eigenfunctions $f_n(\varrho)$ and $p_n(\varrho)$

$$(8) \qquad \varphi(\varrho) = \sum_n \varphi_n(k) f_n(\varrho); \qquad \psi(\varrho) = \sum_n \psi_n(k) p_n(\varrho),$$

where the coefficients φ_n and ψ_n are functions of the momentum variables k. It may be noted that φ_n and f_n as well as ψ_n and p_n need not separately be scalars.

Introducing (8) into (5), multiplying the first Eq. (5) by $f_n^*(\varrho)$, the second by $p_n^*(\varrho)$ and integrating both over the domain of the variables r, we get

$$(9) \quad \begin{cases} (-k_\mu^2 - m_n^2)\varphi_n(k) = \dfrac{g}{(2\pi)^8} \displaystyle\sum_{n'}\sum_{n'''} \int\int M_{n'nn'''}(k', k, k''') \psi_{n'}^*(k') \psi_{n'''}(k''') dk' dk''' \\[2mm] (-k_\mu^2 - \lambda_n^2)\psi_n(k) = \\[2mm] \qquad = \dfrac{g}{(2\pi)^8} \displaystyle\sum_{n''}\sum_{n'''} \int\int M_{nn''n'''}(k, k'', k''') \varphi_{n''}^*(k'') \psi_{n'''}(k''') dk'' dk''', \end{cases}$$

where

$$(10) \quad M_{n'n''n'''}(k', k'', k''') = \int\int\int M(\varrho', \varrho'', \varrho''') p_{n'}^*(\varrho') f_{n''}^*(\varrho'') p_{n'''}(\varrho''') dr' dr'' dr'''.$$

We may now transform Eqs. (9) back into the space of the variables x by means of the transformations

$$(11) \qquad \varphi_n(k) = \int \varphi_n(x) e^{-ik_\mu x_\mu} dx, \qquad \psi_n(k) = \int \psi_n(x) e^{-ik_\mu x_\mu} dx.$$

and finally obtain

$$(\Box - m_n^2)\varphi_n(x) = g \sum_{n'} \sum_{n'''} \int \int M_{n'nn'''}(x',x,x''')\psi_{n'}^*(x')\psi_{n'''}(x''')\,dx'dx'''$$

(12)

$$(\Box - \lambda_n^2)\psi_n(x) = g \sum_{n''} \sum_{n'''}' \int \int M_{nn''n'''}(x,x'',x''')\varphi_{n''}^*(x'')\psi_{n'''}(x''')\,dx''dx'''$$

with

(13) $M_{n'n''n'''}(x',x'',x''') =$

$$= \frac{1}{(2\pi)^{12}} \int \int \int M_{n'n''n'''}(k',k'',k''')\,e^{ik'_\mu x'_\mu + ik''_\mu x''_\mu - ik'''_\mu x'''_\mu}\,dk'dk''dk'''.$$

The set of Eqs. (12) with non-local interaction for the local fields $\varphi_n(x)$ and $\psi_n(x)$ is equivalent with Eqs. (3) for bi-local fields with non-local interaction. The equivalence holds, of course, only under the assumption that (6)−(7) is satisfied and that the eigenfunctions f_n and p_n form a complete set. The formfactor in (12) is given by the original formfactor in (3) and by the eigenfunctions f_n and p_n.

The quantum theory of Eqs. (12) is developed much further [13]−[17] than that of Eqs. (3). Particularly with respect to convergence problems it is more convenient to consider (12) than (3).

Of special importance from the point of view of the possibility of differential quantisation seems to be the case when the interaction in (3) becomes local. This may be achieved by introducing in (3) a sufficient amount of δ-functions. The interaction in (12) may then possibly still remain non-local due to the occurrence of p_n and f_n in the formfactor $M_{n'n''n'''}$. We have then a correspondence between local equations for bi-local fields and non-local equations for local fields. We shall presently consider an example of this type.

Eqs. (3) or (12) are sufficiently general to provide a basis for the discussion of practically all of the modifications of conventional local theory which were proposed so far. In this note we shall consider briefly only the one particular case when the r-space is a Minkowski space (cf. [6] and [7]). The r_α are now co-ordinates of a fourvector. If we assume in accordance with [6] and [7] that they represent co-ordinate differences $(r_\mu = x'_\mu - x''_\mu)$ then the occurrence of r_μ in M^2 and Λ^2 will not violate the principle of translational invariance.

To get Yukawa's example [18] we have to put

(14) $M(\omega',\omega'',\omega''') =$

$$= \delta(r'-x''+x''')\delta(r''-x'''+x')\delta(r'''-x'+x'')\delta[\tfrac{1}{2}(x'+x''')-x''].$$

Eqs. (3) specialise then to

(15)
$$\begin{cases} \left(\dfrac{\partial^2}{\partial x_\mu^2} - \mathbf{M}^2\right)\varphi(x,r) = g\psi^*(x - \tfrac{1}{2}r, -\tfrac{1}{2}r)\psi(x + \tfrac{1}{2}r, -\tfrac{1}{2}r), \\[2mm] \left(\dfrac{\partial^2}{\partial x_\mu^2} - \Lambda^2\right)\psi(x,r) = 2g\varphi(x - r, -2r)\psi(x - 2r, r). \end{cases}$$

They are simple generalisations of Yukawa's equations [18] to the case of two bi-local fields.

Introducing (14) into (12) and assuming that $\mathbf{M}^2$ and Λ^2 and therefore also f_n and p_n are independent on k (as in Yukawa's oscillator model) we get

(16)
$$\begin{cases} (\square - m_n^2)\varphi_n(x) = g \sum_{n'} \sum_{n'''} \int F_{n'nn'''}(z)\psi_{n'}^*(x+z)\psi_{n'''}(x-z)\,dz, \\[2mm] (\square - \lambda_n^2)\psi_n(x) = g \sum_{n''} \sum_{n'''} \int F_{nn''n'''}(-z)\varphi_{n''}(x-z)\psi_{n'''}(x+2z)\,dz \end{cases}$$

with

(17)
$$F_{n'n''n'''}(z) = 2p_{n'}^*(z)f_{n'}^*(-2z)p_{n'''}(z).$$

In (15) and (16) we have an example of two equivalent sets of equations, one of which is a local set for bi-local fields the second being a non-local set for local fields. The question arises as to the possibility of differential quantisation of local equations of the type (15) which differ from the conventional local equations for local fields not only in the appearance of new variables but also in the fact that finite differences of these variables occur. It may be noted also that Yukawa considers the first Eq. (15) and the second Eq. (16) specialised to the case of one bi-local field φ and one local field ψ) as the basis of his considerations. This appears to be inconsistent from the point of view of the general formulation proposed in this note.

Introduction of mass operators depending on k leaves the form of (15) and (16) unchanged. A very interesting example of such an operator was introduced by Markov [19], [20]. The corresponding eigenfunctions possess for time-like momenta a damping factor of the form

(18)
$$\frac{1}{\lambda^2 \pi} e^{\frac{-1}{2\lambda^2}\left[r_\mu^2 - 2\frac{(k_\mu r_\mu)^2}{k_\mu^2}\right]}, \ (k_\mu^2 < 0),$$

where λ is a constant with the dimension of length.

The oscillator model of Markov has the great advantage, as compared with Yukawa's oscillator model, to show only a finite degeneracy. However, as it is immediately seen from (10) and (13), all values of the momenta k occur in the formfactor (13). In order to get a convergent theory it seems therefore of importance to look for an extension of Mar-

kov's model to space-like momenta ($k_\mu^2 > 0$) in such a way as to obtain damping also in this domain. This is connected with the general relativistic (or hyperbolic) eigenvalue problem. The question arises namely if there exist relativistic (hyperbolic) differential operators giving a discrete spectrum of eigenvalues with the corresponding eigenfunctions normalisable in the four-dimensional space. To my knowledge the only example of this kind is Yukawa's oscillator model (mass operator independent on k). This model, apart from its infinite degeneracy, seems trivial since it splits into four independent one-dimensional problems.

The relativistic eigenvalue problem appears also in the relativistic theory of bound states. The corresponding operators contain, of course, always the parameters k, which play the rôle of the momentum of the centre of mass of the system. The explicit solution of this problem is extremely difficult (cf. [21] and [22]) and may be carried out so far only in the case $\vec{k} = 0$. For $k_\mu^2 > 0$ the corresponding equations loose their physical sense.

Thus it is seen that to get simultaneously the solution of the mass spectrum problem and the problem of convergence in frames of the above mentioned theories (with an r-space of Minkowski's type) one has either to choose such formfactors $M(\omega', \omega'', \omega''')$ which prohibit the occurrence of eigenfunctions with space-like momenta (cf. [18], [22] and [6]) or to construct models of elementary particles which provide damping also for $k_\mu^2 > 0$.

Markov's equations for interacting fields [19], [20] may be obtained from (3) by putting

$$(19) \qquad M(\omega', \omega'', \omega''') = \delta(x' - x''')\,\delta(r' - r''')\,\delta(r' - r'')\,\delta(r' - x'' + x').$$

Eqs. (3) become in this case

$$(20) \qquad \begin{cases} \left(\dfrac{\partial^2}{\partial x_\mu^2} - \mathbf{M}^2\right)\varphi(x, r) = g\psi^*(x - r, r)\,\psi(x - r, r) \\[2mm] \left(\dfrac{\partial^2}{\partial x_\mu^2} - \Lambda^2\right)\psi(x, r) = g\varphi(x + r, r)\,\psi(x, r). \end{cases}$$

The second of these equations is just a generalisation of Markov's equation to the case when also the field φ is considered as bi-local.

The corresponding Eqs. (12) become in the particular case (19), if we consider only the simple case when the mass operators $\mathbf{M}^2$ and Λ^2 and, therefore, also the eigenfunctions f_n and p_n do not depend on k,

$$(21) \qquad \begin{cases} (\overline{\square - m_n^2})\,\overline{\varphi_n(x)} = g\displaystyle\sum_{n'}\sum_{n'''}\int F_{n'nn'''}(x - x')\,\psi_{n'}^*(x')\,\psi_{n'''}(x')\,dx', \\[3mm] (\square - \lambda_n^2)\,\psi_n(x) = g\displaystyle\sum_{n''}\sum_{n'''}\int dx''\,\varphi_{n''}(x'')\,F_{nn''n'''}(x'' - x)\cdot\psi_{n'''}(x) \end{cases}$$

with

$$(22) \qquad F_{n'n''n'''}(z) = p_{n'}^*(z) f_{n''}^*(z) p_{n'''}(z).$$

These equations are exactly of the type which was used by the author [13] and by Rayski [14], [15] for the purpose of quantisation of non-local field theories. They give convergence factors only for the free φ-quantum propagation function. One obtains, therefore, (with a proper choice of the formfactor and in the first non-vanishing approximation of the perturbation procedure) a finite result for the self-energy of the ψ-particles, whereas the self-energy of the φ-particles remains unaltered. Introduction of k-dependent mass operators and eigenfunctions seems to be without influence upon this situation.

There are many other models which are contained in the general scheme of Eqs. (3) and (12). One may introduce e. g. mass operators of Pais' type [23]—[26] when assuming the r-space to be a three or four-dimensional Euclidean space. One may also introduce the two-dimensional rotator model of Rayski [8]—[10] or the three-dimensional oscillator model of Markov [19] by assuming the r-space to be the surface of a three-dimensional sphere or a three-dimensional Euclidean space respectively. Another way, which may be more appropriate from the point of view of relativistic invariance, is to start with a four-dimensional Minkowski's space and reduce the number of dimensions by certain subsidiary conditions for the variational principle (1).

We hope to come back to these questions in more detail elsewhere.

THE JOINT INSTITUTE FOR NUCLEAR RESEARCH, DUBNA, USSR

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The ^{121}Sb (n,p) ^{121}Sn Reaction

by

Z. WILHELMI and N. I. PIROGOV

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This paper constitutes a continuation of our investigations of re-
actions of the type (n,p) [1], [2]. The object of those investigations was
to measure the relative cross-section of the reaction ^{121}Sb$(n,p)^{121}$Sn, which
has hitherto not been known. This reaction is of interest in view of the
magic number of protons in the final nucleus $(Z = 50)$.

In measuring the relative cross-section, we used ^{56}Fe$(n,p)^{56}$Mn as
the reference reaction. Metallic antimony of a high degree of purity and
without any trace of tin was irratiated, together with iron, by fast neu-
trons having a continuous energy spectrum up to 14.8 MeV (the neutrons
were derived from the ^{9}Be$(d,n)^{10}$B reaction produced by 10.6 MeV deu-
terons).

In order to ensure identical conditions for irradiation of the iron
and the antimony, both these metals were placed in a closely defined
geometry in the vicinity of a beryllium target. They constituted a kind
of "sandwich" formed by placing thin layers of iron and antimony one
on top of the other.

In irradiating the antimony by neutrons of medium energy, it is
only reactions of the type (n,p) which can lead to the formation of the
nucleide ^{121}Sn. The task of discovering the new reaction we were seeking,
and measuring its cross-section was thus reduced to seeking the isotope
^{121}Sn among the products of the various reactions taking place in the
mass of irradiated antimony, and to measuring the quantity of such
isotope. In view of the small cross-section expected for this reaction,
we built a special target permitting ample irradiation of the antimony
inside the cyclotron. In the test experiments, radioactive isotopes of
antimony, which arose during the irradiation of the antimony by fast
neutrons, made very difficult the observation of the ^{121}Sn sought for.
Therefore, we decided on the chemical separation of the tin atoms ari-
sing in the irradiated antimony as a result of the (n,p) reaction, even

though the separation of tin from antimony itself involves certain known difficulties. We used the following method: Antimony was irradiated in the cyclotron. It was then dissolved in concentrated HCl with an addition of a certain amount of tin as a carrier. After being treated several times with powdered iron, the metallic antimony was precipitated out [10]. The tin in the residual solution was oxidized with hydrogen peroxide to a group IV valence, and precipitated out by means of hydrogen sulphide. The precipitate SnS_2 was dissolved in 70 % $HClO_4$; the solution was heated until it started giving off the white $HClO_4$ vapour, and then diluted in ten parts of water. Hydrolysis gave a precipitate of tin hydroxide [11]. Part of this substance was transferred in the form of a tin layer (0.057 g./cm.²) to a standard dish, and set under the counter. This enabled us to obtain the radioactive decay curve (Fig. 1). Analysis of this
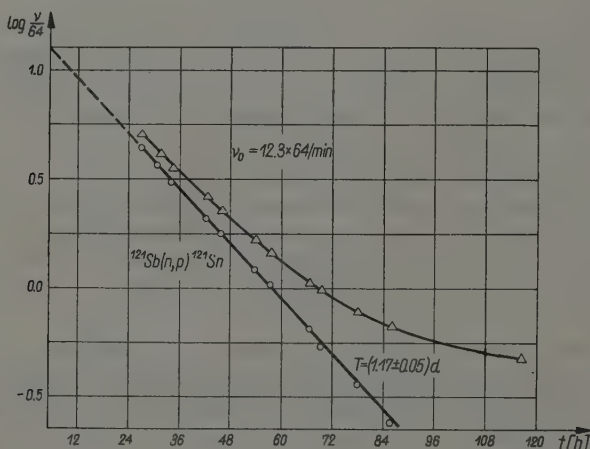

Fig. 1

curve indicated the presence of an isotope with a half-period of (1.17 + + 0.05) days, which we identified as the isotope ¹²¹Sn known from other reactions [4], [5]. In [6] the value obtained for the life of this isotope was (1.1 ± 0.05) days.

In order to better establish as ¹²¹Sn the identity of the isotope observed, and thus to provide stronger confirmation of the existence of the reaction ¹²¹Sb(n,p)¹²¹Sn, we determined the maximum energy of this isotope by an absorption method. The measurements gave us the value $E_{\beta\,max} = (0.48 \pm 0.10)$ MeV, which was in agreement, within the limits of error, with the value of $E_{\beta\,max} = 0.4$ MeV found by Lindner and Perlman [7] for the isotope ¹²¹Sn.

The relative cross-section of the reaction observed (calculated in relation to the reference reaction $^{56}\text{Fe}(n,p)^{56}\text{Mn}$) was found from the following equation:

$$\frac{\sigma_1}{\sigma_2} = \frac{W_{\infty 1} I_2 N_2}{W_{\infty 2} I_1 N_1},$$

where the indices 1 and 2 refer to antimony and iron, respectively:

σ is the cross-section;

I is the mean neutron flux penetrating the given sample;

N is the number of nuclei in the sample;

W_∞ is the corrected initial activity determined by

$$W_\infty = \frac{k \nu_0}{1 - \exp(-0.693\,\tau/T)}.$$

Here τ is the time of irradiation of the sample by neutrons; T is the half-life of the isotope formed; ν_0 is the initial activity — i. e., the number of β particles registered by the counter and extrapolated to the time the irradiation ended; $k = \dfrac{f_0 f_a}{\eta f_b \alpha}$ is the coefficient, taking into account the efficiency of the counter (η), the absorption of particles in the window (f_0) and in the sample itself (f_a), the backscattering (f_b) and, in the case of antimony, the loss of isotope ¹²¹Sn during the chemical treatment (α). The absorption and backscattering were determined by the method described in a previous paper [1], the absorption factor being taken in accordance with the work by Glendenin [8], and the backscattering factor from Burtt [9].

The loss of isotope ¹²¹Sn during the chemical separation from the irradiated antimony was determined by measuring the tin content in

Fig. 2

the final product of this separation process The procedure was: We took a sample of the final product of the chemical treatment, and irradiated it in the reactor together with a standard made from pure metallic tin. From the ratio of the activity of the sample to the standard, which was found on the basis of the decay curves (Fig. 2), we determined the tin
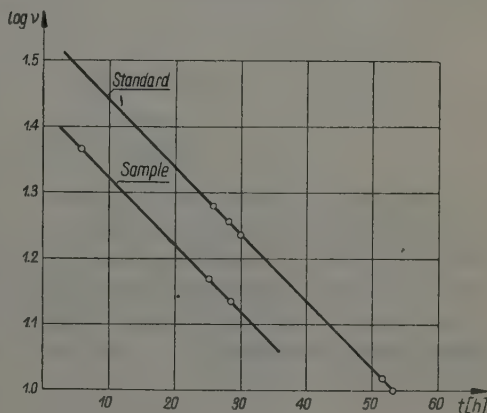
amount in the final product of the sample and the losses during the separation (72%).

All values necessary for calculating the relative cross-section are given in the table below.

TABLE

Sample	Sb	Fe
Isotope investigated	^{121}Sb	^{56}Fe
Mass in the sample of the element under investigation	0.6975 g	0.0115 g
Sample thickness	0.0567 g./cm.^{2}	0.0308 g./cm.^{2}
Irradiation time τ	70 minutes	70 minutes
Initial activity v_0	788 imp./min.	$0.978.10^5$ imp./min.
Abundance of isotope	57.25%	91.64%
Saturated activity $\dfrac{v_0}{1-e^{-0.693\tau/T}}$	2.79×10^4 imp./min.	7.36×10^5 imp./min.
Number of isotope nuclei in sample	1.98×10^{21}	1.336×10^{20}
Chemical treatment loss factor α	0.18	1
Correction factor for absorption of electrons by window f_0	1.18	1.02
Self-absorption factor f_a	3.87	1.36
Backscattering factor f_b	1.6	1.47
Relative neutron flux crossing the Sn- and the Fe-sample, I_{Sn}/I_{Fe}	15.9	0.944
	0.91	

On the basis of these data, it was found that

$$\frac{\sigma^{121}\text{Sn}}{\sigma^{56}\text{Fe}} = 0.040 \pm 0.010.$$

The ratio of these cross-sections was also determined theoretically on the basis of the statistical theory of nuclear reactions. This can be done only with a limited accuracy by an approximation method, since there is, as yet, no accurate data, on the neutron spectrum and the reaction $\text{Be}(d, n)$ at the deuteron energy which we employed. For this approximate calculation, we took the neutron energy as being equal to 14 MeV and found that

$$\left(\frac{\sigma^{121}\text{Sn}}{\sigma^{56}\text{Fe}}\right)_{\text{theor.}} = 0.055,$$

which is not in disagreement with the result obtained experimentally.

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Surface Tensions and Electric Potentials on the Free Surface of Aqueous Solutions of a Wetting Agent

by

J. JANIKOWA

Presented by B. KAMIEŃSKI on January 2, 1957

On the free surface of aqueous solutions one may observe, besides the surface tensions depending on the composition of a solution, also electric potential acting vertically to the surface. The difficulties encountered in experimental work aimed at obtaining measurements of electric potential on the free surfaces were the reason why this line of scientific research was abandoned by many laboratories. The theoretical basis of this phenomenon is, however, rather interesting. Therefore, having overcome the experimental difficulties, the present author has made some measurements of tensions existing on the surface of the octyl ester of sulphosuccinic acid, which is a particularly surface-active substance.

In a previous paper [1], concerning electric potentials and surface tensions of aqueous solutions of other esters of succinic acid known as Aerosols, the influence of the concentration of esters and of the length of the hydrocarbonic acid chain of the investigated esters on the electric potential and on the surface tension was analysed. It was found that the potential as well as the surface tension values in higher concentrations of the investigated compounds (0.01 m.) approached asymptotically the value of 460 mV but 1-σ approached the value of 0.708, which appeared to correspond to the state of surface saturation by polar molecules of the esters. 1-σ denotes the percentage change of surface tension divided by 100. It was also found that the CH_2 groups of the hydrocarbonic chain exerted a distinct influence on the investigated values, particularly with respect to solutions, the concentration of which did not effect desaturation of the surface.

In the present experiment the surface tension and the electric potential of Aerosol OT in various concentrations of hydrogen ions and in various concentration of potassium chloride were examined.

Changes in surface properties below pH 2 were clearly observed in all esters previously investigated in [1] as well as in the Aerosol OT. B. Kamieński and J. Inglot [2]—[6], in their work on the influence of the concentration of hydrogen ions on the potential present on the solution/air interface, have determined that hydrogen ions do not change the electric potential in a solution within the limits of pH 2 to pH 12. Hence, it was necessary to determine the influence exerted by a change in hydrogen ion concentration on the potential of pure solvent (KCl) in its various concentrations.

The potential values were measured by means of a device described by B. Kamieński [2]—[6], the changes in surface tensions — stalagmometrically, and the hydrogen ion concentration – potentiometrically, by application of the Michaelis system [7].

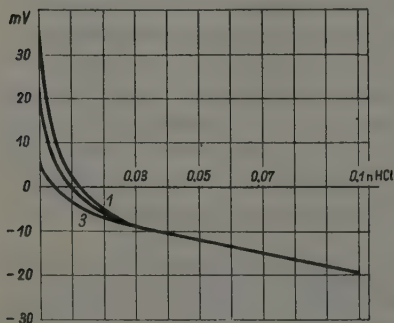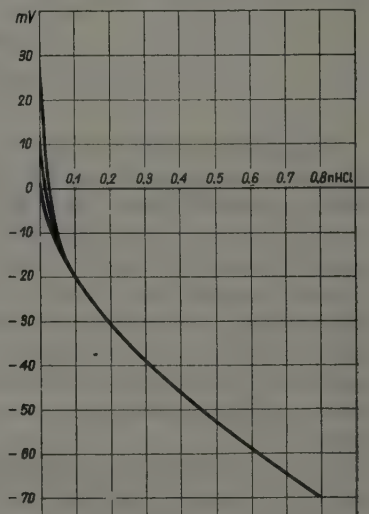Fig. 1 illustrates the dependence of electric potential on the

Fig. 1a

Fig. 1b

concentration of hydrogen ions. Curve 1 represents 0.001 N KCl, curve 2 — 0.01 N KCl and curve 3 — 0.1 N KCl. These curves clearly indicate that, within the limits of pH 6 to pH 1.6, the value of the potential depends on the concentration of potassium chloride, and below pH 1.6 (from the point of meeting to the end of the diagram, in Figs. 1a and 1b) the concentration of potassium chloride had no influence whatever on the value of the potential, and the only cause of the change in the potential was the change in concentration of hydrogen ions.

Fig. 2 illustrates the dependence of surface tension on the concentration of potassium chloride with respect to various concentrations of Aerosol OT. Curve 1 refers to 0.0005 and curve 2 to 0.0001 molar solution of Aerosol OT. It may be noted from the curves that the higher
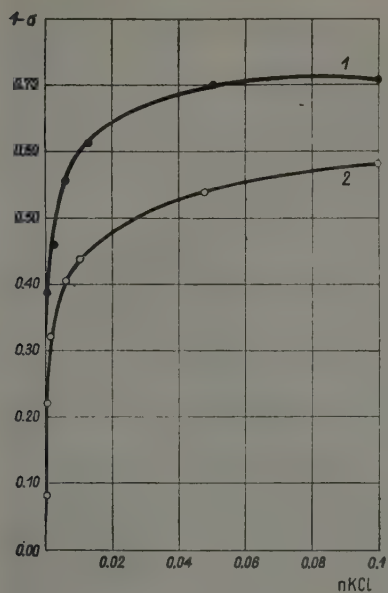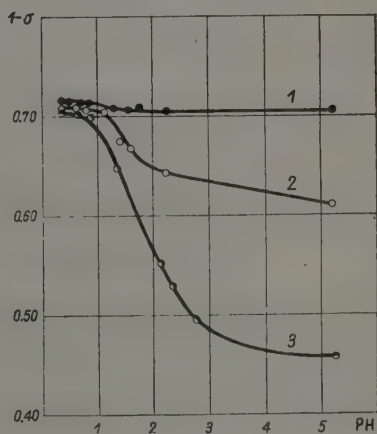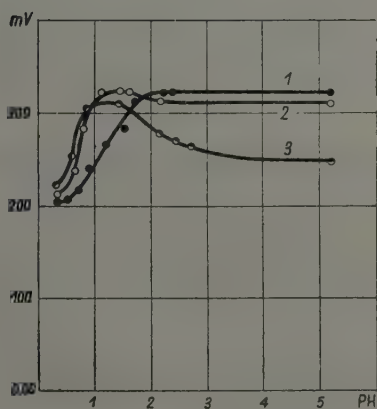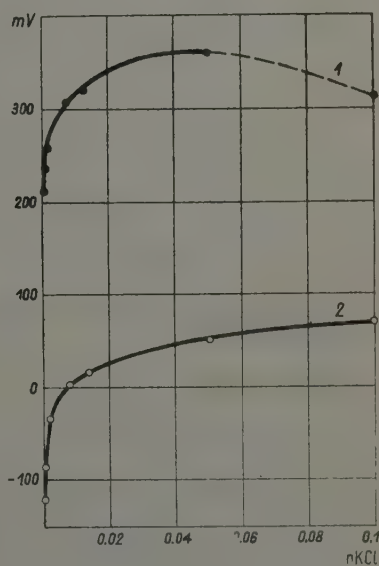
Fig. 2

Fig. 3

Fig. 4

Fig. 5

the concentration of potassium chloride, the stronger is the influence of Aerosol on the surface tension. Fig. 3 represents the dependence of the surface tension on the concentration of hydrogen ions with respect

to 0.0005 molar solution of Aerosol OT in various concentrations of potassium chloride (curve 1 represents 0.1 N, curve 2 — 0.01 N and curve 3 — 0.001 N KCl). As can be seen from the curves, surface tension decreased as the acidification of the solution increased. Only by the highest concentration of potassium chloride did the surface tension change slightly. On comparing the data with those obtained in [1] it was found that the state of saturation on the surface was reached.

The course of the electric potential curves is, however, somewhat different. Fig. 4 illustrates the dependence of electric potential on the concentration of hydrogen ions in Aerosol OT in various concentrations of potassium chloride (curve 1 refers to 0.1, curve 2 to 0.01 and curve 3 to 0.001 of normal KCl). Fig. 5 illustrates the dependence of electric potential on the concentration of potassium chloride in various concentrations of Aerosol OT (curve 1 refers to 0.0005 and curve 2 to 0.0001 molar solution). Results obtained indicate that instead of the expected increase, analogous to surface tension changes, there was a decrease of potential in cases o° low pH values in all investigated concentrations of the solvent. The decrease of the potential became more marked with the increase of the concentration of potassium chloride. This fact indicates that there appears to be a considerable influence of ions on the electric potential when their concentration surpasses a certain value, regardless of the presence of a capillarly active substance.

Summary

Measurements were made of the surface and of the electric potential of aqueous solutions of the octyl ester of sulphosuccinic acid on the air/solution interface with respect to their dependence on the concentration of hydrogen ions and potassium chloride. This ester, known as Aerosol OT, was found to be particularly surface-active even in very dilute solutions. Strong influence of hydrogen ions on the surface and the electric potential was determined.

DEPARTMENT OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, JAGELLONIAN UNIVERSITY, CRACOW

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Vibration Spectrum of Carbonyl Cyanide

by

A. TRAMER and K. L. WIERZCHOWSKI

Presented by W. KEMULA on January 7, 1957

Carbonyl cyanide $CO(CN)_2$ is one of the few molecules with conjugated $C=O$ and $C\equiv N$ bonds. The effect of this structure is a strong chemical and photochemical reactivity [1], [2]. The object of this work is to analyse the structure of the molecule on the basis of the vibration spectrum.

Experimental part

The absorption spectrum of vapours in the infra-red region and the Raman spectra of liquid was obtained for carbonyl cyanide. The pure substance was distilled *in vacuo* before every measurement directly into the absorption cell or Raman vessel. Analysis of the spectra did not indicate the presence of the dissociation products: $(CN)_2$, HCN, CO, CO_2.

The infra-red absorption spectrum of the $CO(CN)_2$ vapours was determined in the range of 2.5 to 14 μ, by a D209 Hilger two-beam prismatic spectrometer with NaCl optics; the vapour pressure was 10 to 120 mm. Hg and the optical path 20 cm. long (Fig. 1). The results of the measurements are shown in Table I. The ac-

Fig. 1a

curacy of the determination of the band position is estimated at 5 cm.$^{-1}$ in the 700-1750 cm.$^{-1}$ range and 20 cm.$^{-1}$ in the 1750-3500 cm.$^{-1}$ range. We also list the absorption coefficients at the band maximum. They
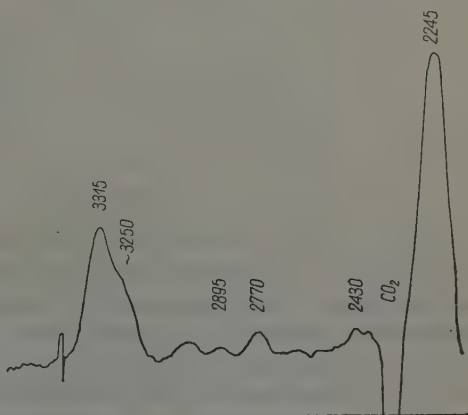
have been calculated by assuming the applicability of perfect gas laws
and the Lambert-Beer law for $CO(CN)_2$ vapours for low pressures. They
are therefore only approximate.
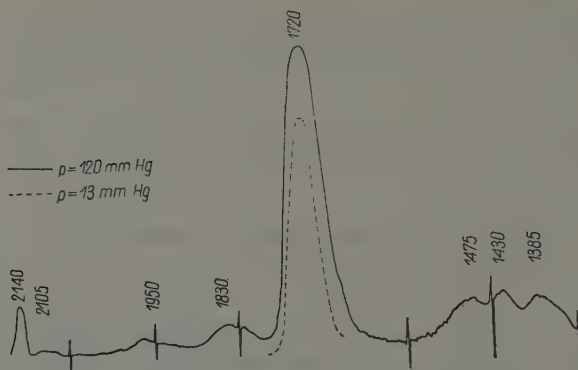
Fig. 1b
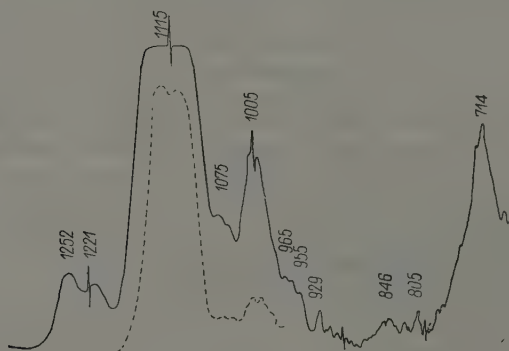
Fig. 1c

The $CO(CN)_2$ molecule no doubt has the structure of an "unsym-
metric top", which makes it possible to distinguish three types of bands
on the basis of the envelope differences. The resolving power of the
instrument enabled us to identify the type B bands (for the notation
see [3]) in some cases only, but did not permit to distinguish the A and C
bands or afford the certainty that all B bands were found (see Table I).

Also investigated was the Raman spectrum in the liquid phase and
in diethyl ether solution of a 32% mole concentration. The measure-
ments were made on an ISP-51 spectrograph with a dispersion of 28 Å/mm.
and on a Huet BII spectrograph with an increased dispersion of 9 Å/mm.
in the blue part of the spectrum.

The spectrum is given in Table II. The accuracy of the frequency determinations is 2 cm.$^{-1}$ for strong lines and 10 cm.$^{-1}$ for weak lines. The notations of strong-line intensities refer to the ether solution and are given with respect to the ether line of 1453 cm.$^{-1}$ frequency.

TABLE I

$CO(CN)_2$ Infra-red spectrum

ν cm.$^{-1}$	I $k \cdot 10^2$	type	ν cm.$^{-1}$	I $k \cdot 10^2$	type
714	10.0 ± 1.0	A	1430	$1.05 + 0.1$	—
805	$w.$	—	~1475	~1	—
846	$w.$	—	1720	41.0 ± 6.0	A(?)
929	$v. w.$	—	1830	0.6 ± 0.1	—
~955	$v. w.$	—	1950	0.3 ± 0.05	—
~965	$v. w.$	B(?)	2105	0.2 ± 0.05	—
1005	6.7 ± 0.1	B	2140	1.5 ± 0.5	A or C
1075	$w.$	B	2245	~46	—
1115	~100	B	2430	~0.5	—
1221	1.4 ± 0.6	—	2770	~0.5	—
1252	2.1 ± 0.35	—	2895	~0.2	—
1385	0.9 ± 0.15	—	3250	$w.$	—
			3315	~2.0	—

TABLE II

Raman spectrum of $CO(CN)_2$

ν cm.$^{-1}$	I	ν cm.$^{-1}$	I
142	15 (vb)	565	$w.$
255	10 (s)	710	10 (b)
306	7 (b)	1709	35 (s)
475	$v. w.$	2108	$w.$
520	$w.$	2248	20 (b)

Assignment of the frequencies

The assignment of the frequencies with respect to the valence vibrations (Table IV) on the basis of the intensity and contour of the bands and comparison with compounds of a similar structure does not raise any doubts. As in the case of malonitrile [4] the symmetric and antisymmetric vibrations of the $C \equiv N$ group are degenerate. The weak Raman 2109 cm.$^{-1}$ line probably corresponds to the difference transition $\nu_{1.6} - \nu_5$. The large reduction of the $C-C$ frequency is, as in the case of other molecules of this type, the result of interactions with the vibrations of other bonds.

The theory envisages the presence in the range of 100 to 600 cm.$^{-1}$ of seven deformation frequencies $(2A_1 + 2B_1 + 2B_2 + A_2)$. Six of them are observed in the Raman spectrum. Analysis of the overtone and combination bands in the absorption spectrum in the infra-red (see Table III) permits nearly all observed bands to be interpreted as simple summation and difference transitions. At the same time, when use is made of the selection rules in infra-red for the C_{2v} symmetry, this analysis excludes the symmetry A_2 for all the observed frequencies. The missing frequency would therefore have to have the symmetry A_2 and would correspond to non-planar vibrations of the $C-C \equiv N$ angle, whose frequency lies in the range 350-400 cm.$^{-1}$. Analysis of the 929 and 1475 cm.$^{-1}$ bands seems to indicate the presence of the 370 cm.$^{-1}$ frequency, for which the symmetry A_2 would be allowed.

TABLE III

Analysis of overtone and summation bands

ν cm.$^{-1}$	interpretation	species	ν cm.$^{-1}$	interpretation	species
805	$\nu_4 + \nu_9$	B_1	1254	$\nu_5 + \nu_7$	B_1
846	$\nu_2 + \nu_5$	A_1	1385	$3\nu_{11}(?)$	B_2
	$\nu_8 + \nu_9$		1430	$2\nu_3$	A_1
929	$2\nu_{11}$	B_2	~1475	$\nu_7 + \nu_{10}$	B_2
	$\nu_8 + \nu_{10}$	A_1	1830	$\nu_3 + \nu_7$	B_1
~955	$\nu_3 + \nu_{12}$	B_2	1950	$\nu_3 + \nu_{12}$	B_2
~965	$\nu_7 - \nu_5$	B_1	2105	$\nu_{1.6} - \nu_5$	A_1, B_1
1005	$\nu_3 + \nu_9$	B_1	2140	$\nu_3 + \nu_{11}$	B_2
1075	$\nu_4 + \nu_8$	B_1	2430	$\nu_3 + \nu_3$	A_1
1221	$\nu_3 + \nu_2$	A_1	2770	$\nu_{1.6} + \nu_{11}$	A_1, B_1
			3315	$\nu_{1.6} + \nu_7$	A_1, B_1

TABLE IV

Fundamentals of $CO(CN)_2$

	co-ordinate species	ν cm.^{1}			co-ordinate species	ν cm.$^{-1}$	
		IR$_{vap}$	R$_{liq}$			IR$_{vap}$	R$_{liq}$
ν_1	$q_N(A_1)$	2245	2248	ν_7	$Q(B_1)$	1115	—
ν_2	$q_0(A_1)$	1720	1709	ν_8	$\delta(B_1)$	—	565
ν_3	$Q(A_1)$	714	710	ν_9	$\omega(B_1)$	—	306
ν_4	$\gamma, \omega(A_1)$	—	520	ν_{10}	$\varphi(A_2)$	(370)	—
ν_5	$\gamma, \omega(A_1)$	—	142	ν_{11}	$\varrho, \varphi(B_2)$	—	475
ν_6	$q_N(B_1)$	2245	2248	ν_{12}	$\varrho, \varphi(B_2)$	—	255

The assignment of the frequencies to the individual normal vibrations was made on the basis of: intensity in the Raman spectra; analysis of the overtone and summation band selection rules; band envelopes; and comparison with the spectra of molecules of similar structure. From the analysis of the electron spectra of $CO(CN)_2$, [6], it follows that the strong 142 cm.$^{-1}$ line shows the symmetry A_1. This is the line characteristic for nitriles [4]. The type B contour of the 1005 and 1075 cm.$^{-1}$ bands indicates that the vibration of frequency 306 cm.$^{-1}$ has the symmetry B_1, and the frequencies 520 and 565 cm.$^{-1}$ are vibrations in the plane of the molecule (A_1 or B_1). Two vibrations of symmetry B_2 would therefore correspond to the 255 and 475 cm.$^{-1}$ lines. Finally, adoption of the second alternative in the interpretation of the 846 and 929 cm.$^{-1}$ bands would indicate the symmetry A_1 for the frequency 520 cm.$^{-1}$ and B_1 for the frequency 565 cm.$^{-1}$. The considerable differences in intensity between the deformation frequencies of the same symmetry can be supposed on the basis of the model, assuming the additiveness of the bond polarizabilities [7].

Such an assignment of frequencies (Table IV) is in agreement with our general conclusions in interpreting the nitrile spectra [4] and with the calculation of the frequency of the $CO(CN)_2$ vibrations on the basis of the force constants determined from the nitrile spectra [5].

We wish to express our thanks to Professor W. Kemula for his constant interest in this work and to Professor O. Achmatowicz for making samples of carbonyl cyanide available to us.

INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES
INSTITUTE OF INORGANIC CHEMISTRY, WARSAW UNIVERSITY

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The Structure of Carbonyl Cyanide

by

A. TRAMER and K. L. WIERZCHOWSKI

Presented by W. KEMULA on January 7, 1957

In this paper we have calculated the force constants of the chemical bonds of carbonyl cyanide on the basis of its vibration spectrum [1] and the assembly of force constants calculated for saturated and unsaturated nitrile molecules [2] in order to form conclusions regarding the character of the chemical bonds of this molecule, and especially the C−C bond. The interpretation of the vibration spectrum is confirmed.

Calculation of force constants

The $CO(CN)_2$ molecule shows a C_{2v} symmetry. Twelve of its normal vibrations can be represented by the equation $Q = 5A_1 + 4B_1 + 1A_2 + 2B_2$. The geometrical parameters of the carbonyl cyanide molecule are not known. For this reason, in making the calculations, theoretical values were used for the angles. The lengths of the bonds were taken as being equal to the lengths in molecules containing a similar bond system, that is, for the C=O bond the length was taken from acetone, and for the C−C and C≡N bonds, from unsaturated nitrile molecules [2], [3], (Fig. 1).

With an assumed valence force model the calculations were made by the method of Volkenstein, Elyashevich and Stepanov [4]. The group of force constants satisfying the secular equations of similarly constructed nitrile molecules [2] was introduced into the calculations. The secular equations were solved by the successive diagonalisation method. The valence force model adopted is illustrated
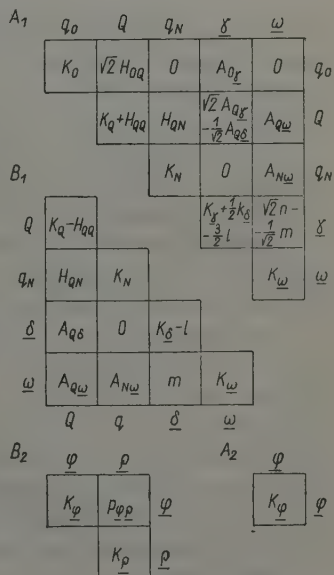

Fig. 1

by the force constant matrices in Fig. 2. The co-ordinate notation is given on the schematic diagram of the molecule.

It turns out that the force constants of nitrile [2] and acetone [5] introduced into the secular equations for types A_1 and B_1 symmetry, satisfy these equations in the zero approximation. The frequency (A_2), being the unknown of the first-degree equation obtained directly by substitution of the value angle ω force constant $(K_\omega = K_\varphi = 0.45 \times 10^6 \text{ cm.}^{-2})$ into the secular equation, has the value 375 cm.$^{-1}$, thus confirming the interpretation of the 370 cm.$^{-1}$ frequency appearing in summation transitions in the infra-red spectrum [1]. Consequently, the secular equation for type B_2 symmetry can be solved with respect to the unknown values of the force constants K_ϱ and $p_{\varphi\varrho}$ by assuming that the interpretation of the frequencies ν_{11} and ν_{12} is correct.

$q_0 = 1.16 \text{Å}$ $\gamma = \delta = 120°$
$q = 1.17 \text{Å}$ $\omega = \varphi = 180°$
$Q = 1.49 \text{Å}$ $\rho = 180°$

Fig. 2

We therefore obtained full confirmation of the interpretation made for the vibration spectra of $CO(CN)_2$ [1].

The force constants were determined more accurately by a variation method. The values obtained for the force constants, and the observed and calculated frequencies are given in Table I.

Character of the $CO(CN)_2$ bonds

Comparison of the force constants of unsaturated nitriles with the force constants calculated for the $CO(CN)_2$ molecule leads to the conclusion that the force field in all these molecules is shaped similarly and is characterised by the conjugation of the $C=C$ or $C=O$ bond with a $C\equiv N$ bond, which is expressed in the increased value of the force constant K_Q with respect to the aliphatic bond $C-C$, and in a small reduction of the constant K_N with respect to aliphatic nitriles. The conjugation is even somewhat stronger in the $CO(CN)_2$ molecule. This is indicated by the force constant of the $C-C$ bond, namely, $K_Q = 8.7 \times 10^6 \text{ cm.}^{-2}$ (in unsaturated nitriles $K_Q = 8.5 \times 10^{-6} \text{ cm.}^{-2}$).

The appearance of a strong K-band with a maximum near 3500 Å [6], [7] in the $CO(CN)_2$ spectrum in the near ultraviolet region confirms the fact that the bonds are conjugated. Similarly, the carbonyl cyanide dipole moment of 1.8 D [8] or 1.38 D [9] — a little larger than the total dipole moments of the $C\equiv N$ and $C=O$ groups — suggests the occurrence of multiple bond conjugation. The small difference between the calculated and experimentally found dipole moment with a doubtlessly occurring induction effect testifies to the fact that the conjugation effect no doubt exists.
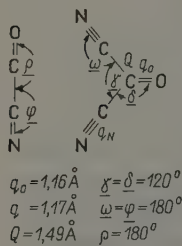
The $C \equiv N$ bond is only insignificantly weakened, and the force constant of the $C = O$ bond undergoes practically no change, similarly to the force constant of the $C = C$ bond in unsaturated nitriles. An increase, in comparison with nitriles, of the interaction between the angles is, however, observed. This is probably connected with the higher symmetry of the $CO(CN)_2$ molecule.

It is obvious that for such a shape of the force field in the $CO(CN)_2$ molecule, the high chemical reactivity of carbonyl cyanide is not connected with some kind of weakening of the $C—C$ bond; here it is even increased as a result of conjugation — but rather with a tendency of the molecule to strongly polarize under the influence of molecules of the medium, which leads to the predominance of the induction effect over the conjugation effect.

We wish to express our thanks to Professor W. Kemula for the interest shown in this work.

TABLE I

Species co-ordinate	Frequency $(cm.^{-1})$		Force constants [in 10^5 cm.$^{-1}$]			
	obs. (R)	calc.				
A_1						
q_v	1709	1708	$K_0 =$	17.5	$A_{0\delta} =$	0.7
Q	710	700	$K_Q =$	8.7	$A_{Q\delta} =$	0.6
q_N	2248	2245	$K_N =$	27.5	$A_{N\omega} =$	0.5
γ, ω	520	520	$K_\gamma =$	0.65	$A_{Q\gamma} =$	0.9
γ, ω	142	125	$K_\delta =$	0.9	$A_{Q\omega} =$	0.15
B_1			$K_\omega =$	0.45	$H_{Q_0} =$	0.14
Q	1115	1110	$K_\varphi =$	0.45	$H_{QQ} =$	0.05
q_N	2248	2255	$K_\varrho =$	0.26	$H_{NQ} =$	0.5
δ	565	548	$m =$	-0.02	$1 =$	-0.035
ω	306	308	$n =$	0.1	$p_{\varphi\varrho} =$	0.14
A_2						
φ	370 (I. R.)	375				
B_2						
φ, ϱ	475	467				
φ, ϱ	255	259				

INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES
INSTITUTE OF INORGANIC CHEMISTRY, WARSAW UNIVERSITY

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Heteroazeotropic Ternary Systems. I.

by

J. STECKI

Presented by W. ŚWIĘTOSŁAWSKI on January 22, 1957

The phenomenon of heteroazeotropy [1] may be often encountered in those systems, in which partial miscibility occurs in the liquid state. Vapour liquid equilibria in heteroazeotropic and heterozeotropic systems have already been examined [2], [3]; however, only qualitative conclusions have as yet been reached. The present paper is an attempt to find certain quantitative relations in this field. However, the whole equilibrium surfaces of the ternary system are not taken into consideration, and only the heteroazeotropic point is examined.

In the binary systems the composition of the heteroazeotrope is simply the composition of the vapour coexisting with two liquid phases (saturated liquid solutions). The boiling temperature of the heteroazeotrope is determined by the total vapour pressure of the two-liquid phase system. The ternary three-phase systems are bivariant; accordingly, at a constant temperature, the compositions of the mutually saturated solutions under the equilibrium pressure are represented by the turbidity curves. These may be approximately identified with binodal curves, which are defined at constant pressure conditions. The shapes of the binodals, as well as the slopes of the tie-lines, are determined by the conditions of thermodynamic equilibrium between the two liquid phases. Consequently, we may write

$$(1) \qquad \mu_1(T, x_2', x_3') = \mu_1(T, x_2'', x_3''),$$

$$(2) \qquad \mu_2(T, x_2', x_3') = \mu_2(T, x_2'', x_3''),$$

$$(3) \qquad \mu_3(T, x_2', x_3') = \mu_3(T, x_2'', x_3'').$$

In these equations μ_i stands for the chemical potential of component "i", T is the absolute temperature, x_i' and x_i'' — the mole fractions of the component "i" in two liquid phases. In terms of activities, de-

fined by the equation

(4) $a_i \equiv x_i \gamma_i \equiv \exp\left[(\mu_i - \mu_i^0)/RT\right],$

in which μ_i^0 is the chemical potential of the pure liquid species "i" at the considered temperature, the Eqs. (1)—(3) become

(5) $a_1(T, x_2', x_3') = a_1(T, x_2'', x_3''),$

(6) $a_2(T, x_2', x_3') = a_2(T, x_2'', x_3''),$

(7) $a_3(T, x_2', x_3') = a_3(T, x_2'', x_3'').$

In principle, these equations might have been solved for an assumed form of dependence of activities on concentration, and an equation should have been obtained for the turbidity lines.

Let us consider the region of the liquid-vapour equilibrium diagram, corresponding to the three-phase systems. At the given temperature the total vapour pressure and the vapour composition vary continuously if both the liquid compositions vary along the turbidity curve. It may happen and, in fact, it happens very often that the total vapour pressure of the saturated solutions passes through a maximum.

From the generalised Gibbs-Konovalov theorem [4] it results that, in a three-phase system, under the condition

(8) $\delta P = 0 \quad (T = \text{const.}),$

the following determinant vanishes:

(9) $\begin{vmatrix} x_1' & x_1'' & y_1 \\ x_2' & x_2'' & y_2 \\ x_3' & x_3'' & y_3 \end{vmatrix} = 0.$

The symbol y_i represents the mole fraction of component "i" in the vapour phase. This condition expresses the fact that, in the triangular diagram, the three points H', H'', Y_H, representing the three phases shall lie on a straight line. If, in addition,

(10) $x_i' < y_i < x_i'',$

the point of maximum vapour pressure is the real heteroazeotropic point, since the two liquids may be again obtained by complete condensation of coexisting vapour. In that case, none of the ternary mixtures, composed of the two liquid phases P' and P'', may be separated by means of the distillation. The corresponding tie-line on which the point lies, representing the composition of the heteroazeotrope, is called the heteroazeotropic line [1]. The vapour compositions y_i, satisfying (9) and (10), are thus the mole fractions of the components in the heteroazeotrope.

Therefore, either Eqs. (9) and (1)−(3), or (9) and (5)−(7) provide a basis for a direct calculation of the compositions and vapour pressures of the ternary heteroazeotropes. It remains to replace y_i by the well known expression

$$(11) \quad y_i = p_i^0(T)\,a_i(T, x_2', x_3')/P(T, x_2', x_3') = p_i^0(T)\,a_i(T, x_2'', x_3'')/P(T, x_2'', x_3''),$$

in which

$$(12) \qquad\qquad P = \sum p_i^0 a_i \quad (i = 1, 2, 3)$$

represents the total vapour pressure, and $p_i^0(T)$ — the vapour pressure of the pure component "i". We next have to solve for x' and x'' the set of equations obtained, and then to introduce the x values into Eq. (11).

Even if the simplest known relations between the activities and the concentrations are accepted, considerable difficulties have to be overcome in applying the method just outlined. Therefore, we have tried to obtain quantitative relations by introducing some arbitrary assumptions. The relations obtained are valid only for a limited number of systems.

We confine ourselves to those systems, in which components 1 and 3 are partially miscible; component 2 has an intermediate value of internal pressure and it is miscible in all proportions with 1 and with 3. Further, we consider only those systems in which the mutual solubility of components 1 and 3, in a binary system, is so small that it may be accepted as equal to zero. The basic assumption is that in those systems it is permissible to neglect the homogenisation effect, and, therefore, to consider the ternary system as an assembly of two binary solutions of 2 with 1 and of 2 with 3. In this extreme case the two branches of the binodal curve coincide with the two respective sides, 1-2, and 2-3, of the concentration triangle. A certain justification of this assumption may be found in the fact that in the case of complete immiscibility in the binary system (1, 3), the tangents of the binodal curve at the points $x_1 = 1$, and $x_3 = 1$, merge with the corresponding triangle sides. It follows that in the case considered, there exists at least a region of compositions (small x_2), in which the assumption introduced is approximately fulfilled.

The following relations are therefore accepted:

$$(13) \qquad\qquad x_1' + x_2' = 1; \quad x_3' = 0,$$

$$(14) \qquad\qquad x_2'' + x_3'' = 1; \quad x_1'' = 0.$$

Condition (9) reduces to the following:

$$(15) \qquad\qquad \begin{vmatrix} 1 - x_2' & 0 & y_1 \\ x_2' & x_2'' & y_2 \\ 0 & 1 - x_2'' & y_3 \end{vmatrix} = 0.$$

It may be rewritten as

$$(16) \qquad (y_1/y_2)\frac{x'}{1-x'} + (y_3/y_2)\frac{x''}{1-x''} = 1.$$

In addition, let us assume that the ternary heteroazeotropes behave as regular mixtures.

In that case

$$(17) \qquad RT \log \gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + x_2x_3(A_{12}+A_{13}-A_{23}),$$

$$(18) \qquad RT \log \gamma_2 = A_{12}x^2 + A_{23}x^2 + x_1x_3(A_{12}+A_{23}-A_{13}),$$

$$(19) \qquad RT \log \gamma_3 = A_{13}x_1^2 + A_{23}x_2^2 + x_1x_2(A_{13}+A_{23}-A_{12}).$$

The extreme case corresponds to the conditions:

$$A_{12} < 2\,RT, \qquad A_{23} < 2\,RT, \qquad A_{13} = \infty.$$

Substituting (18) into (6) and taking into account (13) and (14), we obtain

$$(20) \qquad x' \exp[\beta_{12}(1-x')^2] = x'' \exp[\beta_{23}(1-x'')^2],$$

in which

$$(21) \qquad \beta_{12} \equiv A_{12}/RT, \qquad \beta_{23} \equiv A_{23}/RT.$$

Eq. (20) enables us to calculate the slopes of the tie-lines. From Eqs. (11), (13), (14), and from (17), (18), (19) the following relations are obtained:

$$(22) \qquad y_1/y_2 = \frac{p_1^0}{p_2^0}\frac{1-x'}{x'}\exp[\beta_{12}(2x'-1)],$$

$$(23) \qquad y_3/y_2 = p_3^0/p_2^0 \cdot \frac{1-x''}{x''}\exp[\beta_{23}(2x''-1)].$$

Equation (16) simplifies to

$$(24) \qquad \frac{p_1^0}{p_2^0}e^{\beta_{12}(2x'-1)} + \frac{p_3^0}{p_2^0}e^{\beta_{23}(2x''-1)} = 1.$$

Because at the binary homoazeotropic points

$$(25) \qquad p_1^0/p_2^0 = \exp[\beta_{12}(1-2x^{(1,2)})]$$

and

$$(26) \qquad p_3^0/p_2^0 = \exp[\beta_{23}(1-2x^{(2,3)})],$$

we can, by eliminating the values of p_i^0, introduce the concentrations of homoazeotropes $x^{(1,2)}$ and $x^{(2,3)}$ into the equations just derived. In this way, relations are obtained involving only the concentrations. Equation (24) becomes

$$(27) \qquad \exp[2\beta_{12}(x'-x^{(1,2)})] + \exp[2\beta_{23}(x''-x^{(2,3)})] = 1,$$

whereas Eqs. (22) and (23) can be rewritten in the form

(28) $$y_1/y_2 = \frac{1-x'}{x'} \exp\left[2\beta_{12}(x'-x^{(1,2)})\right],$$

(29) $$y_3/y_2 = \frac{1-x''}{x''} \exp\left[2\beta_{32}(x''-x^{(2,3)})\right].$$

Let us discuss Eqs. (20), (27), (28), (29). The first two enable us to find the x' and x'' values. After substituting them into (28) and (29), we obtain the y_i values. Unfortunately, it is not possible to solve Eq. (20), or the system of equations (20), (27). The x'' value, corresponding to the given x', may be either calculated by the trial and error method, or found graphically. It is possible, however, to obtain some results by analysing these equations, especially as concerns the series of heteroazeotropes [5]—[7] of the type $(1_i,2,3)$ or $1,2,3_i)$. On the other hand, for the calculation of the composition of the single heteroazeotropes an approximate method has been found, and it will be described in another paper. From the relations just derived, certain conclusions may, however, also be drawn. First of all, it follows from condition (27) that each exponential term does not exceed unity. Therefore

Fig. 1. A typical dislocation of the points characterising the ternary heteroazeotrope. On the heteroazeotropic line $H'H''$ lies the ternary heteroazeotropic point Y_H, $Az^{(1,2)}$ and $Az^{(2,3)}$ being homoazeotropic points, and $H\,Az^{(1,3)}$ the binary heteroazeotropic point.

(30a) $$x^{(1,2)} > x',$$

(30b) $$x^{(2,3)} > x''.$$

If $(x'-x^{(1,2)})$ tends to zero, then $(x^{(2,3)}-x'')$ tends to infinity, and, since $0 < x'' < 1$, $x^{(2,3)}$ tends to reach infinity. Due to Eq. (26), the quotient p_1^0/p_2^0 vanishes; this means that the composition of the binary heteroazeotrope approaches a hundred per cent of "1" (since p_3^0 is finite and not equal to zero). If x'' and $x^{(2,3)}$ become equal to one another, $x^{(1,2)}$ tends to infinity, and $y_3^{(1,3)}$ tends to unity (a hundred per cent of component "3"). It should not be forgotten that the composition of the binary heteroazeotrope is given by the equation

(31) $$y_1^{(1,3)}/y_3^{(1,3)} = p_1^0/p_3^0, \quad y_1^{(1,3)} + y_3^{(1,3)} = 1.$$

In Fig. 1 a typical case is shown, in which the inequalities mentioned above are fulfilled.
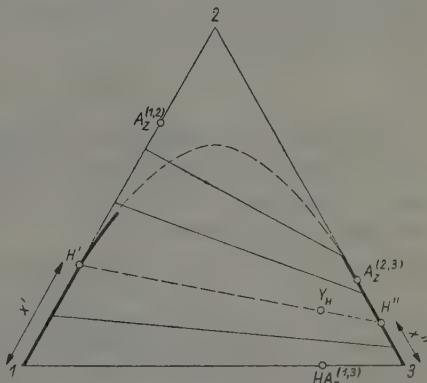
If (30a) and (30b) are taken into account, the conditions

$$y_1/y_2 > (1-x')/x', \quad y_3/y_2 > (1-x'')/x''$$

result directly from Eqs. (28), (29).

Kogan has recalculated the numerical data for ternary heteroazeotropes [8] in order to show that

$$(32) \qquad \left(\frac{X_2}{X_1}\right)_{\text{ternary}} < \left(\frac{X_2}{X_1}\right)_{\text{binary}},$$

$$(33) \qquad \left(\frac{X_2}{X_3}\right)_{\text{ternary}} < \left(\frac{X_2}{X_3}\right)_{\text{binary}}.$$

In fact, all heteroazeotropic systems having binodal curves of the type considered in this paper, fulfil (32) and (33). These inequalities may be deduced from our relations in the following manner. We rewrite (32) and (33) as follows:

$$(34) \qquad y_1/y_2 > (1-x^{(1,2)})/x^{(1,2)},$$

$$(35) \qquad y_3/y_2 > (1-x^{(2,3)})/x^{(2,3)}.$$

Substituting the expression (22) into (34) we obtain

$$(36) \qquad \frac{1-x'}{x'} \exp[2\beta_{12}x'] > \frac{1-x''^{(1,2)}}{x''^{(1,2)}} \exp[2\beta_{12}x^{(1,2)}].$$

Since $x' < x^{(1,2)}$, a sufficient condition for (36) is the decreasing character of function $f(x) = (1-x)(x^{-1})\exp(2\beta x)$. By differentiation we obtain that (36) and (34) are fulfilled, unless

$$2\beta(1-x) - \frac{1}{x} < 0, \quad \text{or} \quad x^2 - x + (2\beta)^{-1} > 0.$$

This is true for all values of x, if $\beta < 2$. If, however, $\beta \geqslant 2$, $f(x)$ has a minimum at the point

$$(37) \qquad x = \frac{1}{2} - \left(\frac{1}{4} - \frac{1}{2\beta}\right)^{1/2}.$$

Therefore, inequalities (34) and (35) are fulfilled with certainty in all cases, except those characterised by such large values of β, that the separation into two layers of systems $(1, 2)$ or $(2, 3)$ may take place. In the cases in which $\beta \geqslant 2$, (34) or (35) still remains true, unless $x^{(1,2)}$ or $x^{(2,3)}$ does not exceed the value resulting from (37).

Summary

1. General conditions are formulated, determining the location of the heteroazeotropic line and the composition of the ternary heteroazeotrope in partially miscible systems.

2. The systems are examined in which one pair (1,3) of the components is completely immiscible, whereas both other pairs, (1,2) and (2,3), form binary systems miscible in all proportions. It is tentatively assumed that in the ternary system the homogenisation is negligible in the region extending from the triangle side 1-3 up to the heteroazeotropic line. This assumption makes it possible to develop quantitative relations which are derived and discussed under the assumption that the liquid phases behave as regular solutions. Several characteristic inequalities are deduced, involving the compositions of binary azeotropes, of the ternary heteroazeotrope, and of the liquid phases forming the latter.

RAW ORGANIC MATERIALS DEPARTMENT OF THE INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES

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The Magnetic Properties of Platinum Catalysts
with γ-Al$_2$O$_3$ as Carrier

by

W. TRZEBIATOWSKI and H. KUBICKA

Presented by W. TRZEBIATOWSKI on January 24, 1957

Platinum catalysts were prepared from solutions of chloroplatinum acid and γ-Al$_2$O$_3$ — both of spectroscopically controlled purity; only the last showed detectable traces of Si ($<10^{-2}\%$) and Mg, Fe, Ga, In, K, Na ($<10^{-3}\%$). The small iron content did not influence the magnetic measurements, because it was not in the ferromagnetic state as follows from the magnetic susceptibility of the γ-Al$_2$O$_3$, which was practically field- and temperature-independent and showed a diamagnetism $\chi_g = -0.33 \cdot 10^{-6}$ at $80°$K. The area of this carrier substance was 280 m.^{2}/g. as determined by the BET method with nitrogen gas at liquid nitrogen temperature. The platinum content of the catalyst was controlled by using suitable quantities of H$_2$PtCl$_6$ solution and determining the platinum balance after filtration of the solution from the carrier, which retained a part of it. The catalysts were reduced with pure hydrogen at $300°$C. during 2 hours and subsequently outgassed at $200°$C. *in vacuo*. Also a portion of pure carrier substance was treated in the same manner, using only redestilled water instead of H$_2$PtCl$_6$ solution. The sample of pure platinum was prepared by reduction of chloroplatinum acid with hydrogen.

The magnetic measurements were carried out in the temperature range between $80°$ and $300°$K. and at the magnetic fields from 2770 to 15560 oe, the methods and apparatus already described [1] being used. The magnetic susceptibilities of all samples investigated were independent of the magnetic field.

The susceptibilities of catalysts and pure carrier substance determined with the accuracy of $\pm 0.03 \cdot 10^{-6}$ were also practically temperature independent.

Magnetic mass susceptibilities of the catalysts $Pt/\gamma\text{-}Al_2O_3$ at room temperature (18-19°C.)

Sample number	Pt-content of catalyst	$\chi_{measured} \cdot 10^6$	$\chi_{calculated} \cdot 10^6$ *)
1	pure platinum	+0.973	—
2	4.1 weight %	−0.31	−0.30
3	2.5 ,,	−0.33	−0.33
4	1.2 ,,	−0.33	−0.34
5	0.2 ,,	−0.37	−0.36
6	pure $\gamma\text{-}Al_2O_3$	−0.36	—

*) calculated from $\chi_{\gamma\text{-}Al_2O_3} = -0.36 \cdot 10^{-6}$ and $\chi_{Pt} = +0.973 \cdot 10^{-6}$.

As shown in the table, no increase in the magnetic susceptibility of the catalysts was observed at the metal concentrations of 0.2 to 4.1% here presented, which correspond to a coverage degree of the carrier surface with monomolecular Pt layers of 0.0015, 0.009, 0.019 and 0.03, respectively. A surface demand of platinum atoms of 6.6 A^2/at. was accepted. This indicated that the magnetic behaviour of platinum supported on $\gamma\text{-}Al_2O_3$ as carrier did not offer such anomalies as those noted by N. I. Kobosev [2]. Results obtained by him indicated susceptibilities of platinum belonging to: $735 \cdot 10^{-6}$ at 0.0017, $1420 \cdot 10^{-6}$ at 0.002 and $5130 \cdot 10^{-6}$ at 0.001 surface coverage of alumogel. These results cannot be explained by the convenient theory of paramagnetism.

DEPARTMENT OF STRUCTURAL RESEARCH, INSTITUTE OF PHYSICAL CHEMISTRY, WROCLAW

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CHEMISTRY

Studies on the Critical Temperature Curves of Mixtures. III. The Effect of Volume Changes by Mixing

by

A. KRĘGLEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on February 14, 1957

Introduction. In a previous paper [3] we concluded that the azeotropic range Z_{ij} of a binary system under low pressures (e. g. 1 atm.) can be calculated in some cases from the critical temperature curve by means of the following equation of Malesiński:

$$(1) \qquad (\sqrt{\delta_i} + \sqrt{\delta_j})^2 = \tfrac{1}{2} Z_{ij},$$

in which δ_i and δ_j are the azeotropic depressions. For applying the relation to the critical temperature curve, i. e., for computing $\tfrac{1}{2} Z_{ij}^c$, the azeotropic depressions should be replaced by the analogous quantities $\delta_i^c = T_i^c - T_{ex}^c$ and $\delta_j^c = T_j^c - T_{ex}^c$, where T_i^c, T_j^c and T_{ex}^c are respectively the critical temperatures of the pure components and of the extremum point on the critical curve (T^c, x).

It has been also shown [3] that the important relation between the azeotropic ranges of three binary regular solutions $(1, 2)$, $(2, 3)$ and $(1, 3)$, derived by Malesiński [4], on the basis of Świętosławski's scheme of formation of ternary azeotropes [1], [2]

$$(2) \qquad \tfrac{1}{2} Z_{12} + \tfrac{1}{2} Z_{23} = \tfrac{1}{2} Z_{13},$$

may also be applied to critical temperature curves.

Relation (2) is applicable only in the absence of specific molecular interactions between unlike molecules of the systems under consideration [5]. By mixing the components, such interactions can lead to the appearance of large volume changes. Usually a volume contraction is observed. We will show that relation (2) is fulfilled in the critical region even in the presence of specific interactions, if a correction for the "excess volume of mixing V^E" is introduced. It seems also possible to explain in the same way the differences between Z_{ij}^c (critical) and Z_{ij} correspon-

ding to the boiling temperature isobars, observed in systems of non-polar molecules; for instance, in the propane-sulphur hexafluoride system [3].

The critical temperature curve of binary mixtures. In 1931 Scatchard [6] derived the equation for the so-called "cohesive energy" of a mole of liquid mixture (essentially its potential energy E, but taken with opposite sign)

$$(3) \qquad -EV = c_{11}V_1^2 x_1^2 + 2c_{12}V_1V_2 x_1 x_2 + c_{22}V_2^2 x_2^2$$

in which c are constants ("cohesive energy densities"), V_1, V_2 and V — molar volumes of the components and of the solution, and x — the mole fractions. For the pure components we have

$$(3a) \qquad -E_1 = c_{11}V_1 \quad \text{and} \quad -E_2 = c_{22}V_2.$$

According to Scatchard's assumption the volume of the solution is additive, i. e.,

$$(3b) \qquad V = V_1 x_1 + V_2 x_2.$$

Scatchard's assumptions made on deriving Eq. (3) in the case of solutions at low temperatures are very crude. In the critical region, however, they are probably better fulfilled owing to the high kinetic energy of the molecules and low density of the fluids.

Recently van Dranen [7] enunciated the hypothesis that "the critical state is the result of the fact, that at the critical temperature T^c the average kinetic energy is equal to the average (negative) potential energy"

$$(4) \qquad -E = \tfrac{3}{2}RT^c \quad (R - \text{gas constant}).$$

From Eqs. (3), (3a) and (4) we obtain the expression for the critical temperature of a mixture

$$(5) \qquad T^c V^c = T_1^c V_1^c x_1^2 + 2\theta_{12}V_1^c V_2^c x_1 x_2 + T_2^c V_2^c x_2^2,$$

where

$$(5a) \qquad \theta_{12} = \frac{2c_{12}}{3R},$$

and the volumes are replaced by molar critical volumes V^c.

If the volumes V_1^c and V_2^c are equal and additive, Eq. (5) simplifies itself to the known relation

$$(6) \qquad T^c = T_1^c x_1^2 + T_{12}^c x_1 x_2 + T_2^c x_2^2,$$

in which $T_{12}^c = \theta_{12}V^c$.

When the critical temperature differences of the components are large, θ_{12} (and also T_{12}^c) is not constant, but changes approximately linearly with the composition of mixture. Therefore the values found at $x = 0.5$ can be assumed as being characteristic for the given system.

The relation between the regular solution constants. The regular solution constant is defined as in [6]:

$$(7) \qquad A_{ij} = c_{ii} + c_{jj} - 2c_{ij}.$$

At the critical point of a system $(1, 2)$ we obtain according to $(3a)$, (4) and $(5a)$

$$(8) \qquad A_{12}^c = \frac{3}{2} R \left(\frac{T_1^c}{V_1^c} + \frac{T_2^c}{V_2^c} - 2\,\theta_{12} \right).$$

Malesiński has shown [3] that

$$(9) \qquad A_{12} + A_{23} = A_{13},$$

where component 2 has, as in relation (2), the medium value of the internal pressure. Since c may be considered as a standard measure of the internal pressure [6], component 2 can be chosen by comparing the $c_{ii} = \frac{3}{2} R T_i^c / V_i^c$ values of the three substances 1, 2 and 3.

Accurate data for the (T^c, x) as well as for the (V^c, x)-curves, available only for few systems, are given in Table I.

TABLE I

Regular solution constants at the critical point (calculated at $x = 0.5$)

| Components | | Reference | V_i^c l/mole | V_j^c l/mole | V^c at $x=0.5$ | T_i^c ⁰K | T_j^c ⁰K | T^c at $x=0.5$ | $2\theta_{ij}$ (Eq.5) | A_{ij} cal. (Eq. 8) | Combination of systems (Eq. 9) |
i	j										
CO_2	N_2O	[9]	0.0939	0.0974	0.0939	304.2	309.5	306.1	6150	800	(1,2)
N_2O	C_2H_6	[8]	0.105	0.143	0.124	309.2	305.2	299.1	4810	800	(2,3)
CO_2	C_2H_6	[8]	0.0986	0.143	0.121	304.4	305.2	291.0	4750	1410	(1,3)
H_2S	CO_2	[10]	0.0977	0.0946	0.0930	373.4	304.3	328.2	6150	2660	(1,2)
CO_2	C_2H_6	[8]	0.0986	0.143	0.121	304.4	305.2	291.0	4750	1410	(2,3)
H_2S	C_2H_6	[11]	0.0984	0.148	0.115	373.1	305.2	323.8	4590	3760	(1,3)

The systems must fulfil certain conditions required for testing relations (9) and (2), namely, relatively large positive deviations from ideal behaviour $(A_{ij} > 0)$, and relatively small critical temperature differences of the components.

The (V^c, x)-curves of the ethane-carbon dioxide and ethane-nitrous oxide systems have such an inflection that the value of V^c at $x = 0.5$ is approximately equal to that calculated from (3b). Additivity of volumes

has been assumed for these systems *). The remaining systems show considerable volume contraction by mixing (excess volume $V^E < 0$).

Table I contains the values of A_{ij} calculated by the use of Eqs. (5) and (8) from experimental data for V_i^c, V_j^c, T_i^c, T_j^c, and for T^c and V^c at $x = 0.5$. The medium value of T_i^c/V_i^c in the first combination shows nitrous oxide, while in the second — carbon dioxide (component 2). Relation (9) is fulfilled within about 10 per cent.

The influence of volume changes by mixing on Z_{ij}^c. If the value of θ_{12} and the critical constants of the components are known, it is pos-
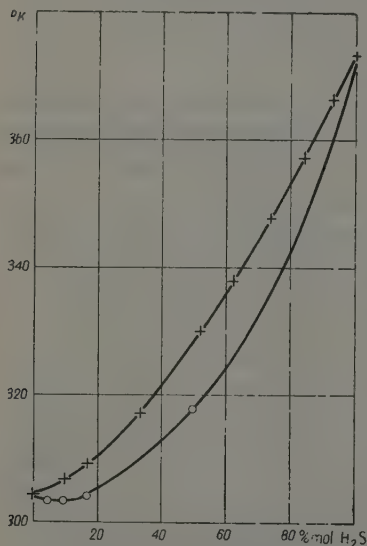

Fig. 1. Critical temperature curves of the hydrogen sulphide-carbon dioxide system. Upper curve — experimental [10], lower curve — hypothetical (for $V^E = 0$).

sible to calculate from Eq. (5) a hypothetical (T^c, x)-curve of the system which could exist if the volumes V^c were additive. According to this equation, the hypothetical values of T^c will be lower than the experimental ones, if $V^E < 0$, or will be higher, if $V^E > 0$ at the given compositions. In order to obtain the hypothetical (T^c, x)-curves of the systems under consideration, the following calculations have been performed: (a) θ_{12}-values, computed from experimental data for T^c and V^c at several compositions by the use of (5), were substituted into the same equation; (b) experimental values of V^c were replaced in (5) by the additive ones (computed from Eqs. (3b)) and (c) the hypothetical values of T^c at these compositions were calculated.

Data for the hydrogen sulphide-carbon dioxide system, showing especially large volume contraction by mixing (due to strong hydrogen bond formation) are given in Table II and are plotted in Fig. 1. This, and also the hypothetical curves of the remaining systems given in Table III, show a minimum which enables to calculate Z_{ij}^c from Eq. (1). The experimental and hypothetical critical curves of the systems formed by ethane with carbon dioxide and nitrous oxide are assumed to be identical (according to our assumption of additivity of experimental critical volumes of these systems).

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*) V_i^c of CO_2 determined by the author cited in International Critical Tables, differs considerably from the two more recent values [9], [10]. The data for (V^c, x)-curve of N_2O—C_2H_6 and CO_2—C_2H_6 systems are probably also inaccurate.

TABLE II

The effect of volume changes by mixing on the critical temperature curve of the system $H_2S—CO_2$

Composition, x_1	0.050	0.099	0.171	0.500
T^c experimental	305.2	306.7	309.16	328.2
V^c experimental	0.0941	0.0938	0.0935	0.0930
$2\,\theta_{12}$ (Eq. 5)	6040	6110	6160	6150
V^c calc. (Eq. 3b)	0.0948	0.0949	0.0951	0.0961
T^c hypothetical	303.0	303.2	304.0	317.5

TABLE III

Values of Z_{ij}^c calculated from the hypothetical critical temperature curves

Component		Combination of systems (Eq. 2)	T_{ex}^c	δ_i^c	δ_j^c	$\frac{1}{2}Z_{ij}^c$ (Eq. 1)	$\frac{1}{2}Z_{12}^c + \frac{1}{2}Z_{23}^c$ (Eq. 2)
i	j						
CO_2—N_2O		(1,2)	300.5	3.7	9.0	24.2	
N_2O—C_2H_6		(2,3)	299.2	10.0	6.0	31.5	55.7
CO_2—C_2H_6		(1,3)	290.8	13.6	14.4	56.0	
H_2S—CO_2		(1,2)	303.0	70.4	1.3	90.8	
CO_2—C_2H_6		(2,3)	290.8	13.6	14.4	56.0	146.8
H_2S—C_2H_6		(1,3)	294	79	11	149.0	

The data given in Table III indicate that the relation (2) is fulfilled much better than was expected. The transformation of real into hypothetical critical temperature curves makes it possible to consider the systems as such in which do not exist specific molecular interactions. It seems that the excess volume of mixing is a certain measure of specific interactions at least in the critical region.

The author is indebted to Professor W. Świętosławski for his assistance in the course of this work.

Summary

An equation for the critical temperature curve (T^c, x) of binary mixtures has been derived on the basis of the van Dranen's hypothesis [7] and Scatchard's expression for the "cohesive energy" of a mixture [6]. It is shown, that the relation between the azeotropic ranges Z_{ij} of the three binary systems (1,2), (2,3) and (1,3) [4]

$$\tfrac{1}{2}Z_{12} + \tfrac{1}{2}Z_{23} = \tfrac{1}{2}Z_{13}$$

when applied to (T^c, x)-curves, is fulfilled even in the presence of strong specific molecular interactions, provided that the correction for the "excess volume of mixing" is introduced. (T^c, x)-curves of hypothetical systems characterised by additive molar critical volumes have been calculated for binary mixtures of N_2O, CO_2, H_2S and C_2H_6.

INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES

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Clay Minerals as Possible Palaeogeographic Indices

by

J. TOKARSKI

Presented on December 2, 1955

Clay minerals which have, thus far, been estimated to constitute 82 per cent of the clastic sedimentary crust of the Earth, are essentially the products of weathering of original magmatic rocks. Hydrolysis is the prime factor of their development; the pattern of its evolution varies, depending on conditions of formation and nature of the weathering material. These minerals occur within vast areas of marine basins of sedimentation and over nearly the whole of the surface of the continents; The outermost part of the Earth's crust, that adjacent to the atmosphere, is an area of their maximum accumulation. It is a zone bearing particular characteristics, well known in science under the name of soil. It has developed at almost all geographical latitudes, though under various potential conditions dependent on climate, morphology of the given terrain and, foremost, on intensity of evolution of the biological processes. Time is also an important factor here. The final result of the dynamics, which accompany processes affecting the soil, is the formation of soil profiles, with differentiated horizons. These horizons consist of various minerals constituents, with various quantitative ratios, the clay minerals being here of importance. An examination of the soil profile will enlarge our knowledge of the history of evolution of the soil.

X-ray, and thermal differential analyses, as also the electronic microscope method, have provided complete data with regard to some of the constituents of clay substance here considered, the separation of the more characteristic units and groups and have, finally, enabled a classification to be made based on sound evidence. The montmorillonite, kaolinite and illite groups have thus now been differentiated. Research studies on the first two of these groups have proved particularly fruitful.

They have namely led to the montmorillonite group being placed in one isomorphic line, together with montmorillonite, beidelite, nontronite and saponite [1]. These links are believed to have the same model

of chemical structure, consisting of four-fold and six-fold co-ordination. The chief cations participating in the formation of such a structure are Si^{+4}, Al^{+3}, Fe^{+3} and Mg^{+2}, together with an unimportant amount of others such as Ca^{+2}, P^{+5}, etc. [1], with 0^{-2} and $(OH)^{-1}$ as anions. The minerals studied here are distinguished by a characteristic platy structure the function of which are all their physical and chemical properties. Where the size of the elements is below 1 micron, a substance is formed, which is classed as the group of "colloids". The chemical composition of a link in any of the groups studied depends on the environment of its formation, particularly on climatic conditions.

The kaolinite group shows the same pattern of chemical structure, differing from montmorillonite minerals only in the arrangement of its atom layers.

The illite group — the least known — belongs structurally to an analogous type, being closest related to minerals of the micaceous group.

Glauconite, regarded as a "typically" marine mineral, is in structure obviously related with the montmorillonite group, particularly with its nontronite link.

All the montmorillonite and glauconite links dissolve in HCl and this is always a feature distinguishing them from the other minerals mentioned here.

From the soil surface of continents, in whose profiles the groups of clay minerals here considered are uninterruptedly forming, altering and disappearing, erosion and denudation are continually washing away enormous masses of colloidal material and transporting it to basins of sedimentation. In time, by way of diagenesis, diverse types of clay components of clastic rocks are formed from this "raw material".

Present knowledge of the nature of these clay elements has been obtained by investigating samples collected from geological deposits with particular care, in an uncontaminated condition. Most of the material studied has been recovered from bentonites, viz. montmorillonite links, genetically connected with the devitrification of volcanic glass in basic magmatic rocks. It has not been possible to isolate any of these clay elements from soil profiles since, as a rule, they form here mixed and strongly bound packets, consisting of diverse elements. Nevertheless, their presence in this environment has been ascertained by different methods of investigation. Furthermore, differences of features noted in soils from different climatic zones are, among others, also being tentatively explained by differences noted in assemblages of elements belonging to the so-called "clay complex". Two cardinal questions arise in this connection, namely, whether clay mineral assemblages formed in soil profiles, varying in every climatic zone and transported from the surface of continents to sedimentary basins by wash-away processes, are metamorphosed in marine environment, or whether they persist there in un-

altered forms of chemical structure. If the second question is answered positively we may obtain sound paleogeographical evidence as a result of our studies on sedimentary rock profiles. For a solution of this problem attention should primarily be turned to analytic comparison of soil clay complexes with their rock equivalents. The present paper contains the first numerical data in this respect, obtained by a theoretical discussion of the problem, as stated below. The fact that montmorillonite and glauconite links readily dissolve in HCl suggested the comparison of extract from soil loam complexes, obtained under the same conditions by treatment in this reagent, with analyses of elements from the montmorillonite and glauconite groups [2]. As a result, 42 of these analyses have been tabulated in the following table. Nineteen of them, viz. Nos. $1-9$, $11-16$, 19, 24, 28 and 42, deal with the montmorillonite-glauconite group. Analyses Nos. $17-18$ and 25 refer to elements from Carpathian rocks; the remainder, Nos. $20-23$, 26, 27, 29, $31-41$, to diverse types of soil profiles in light soil. Two analyses, Nos. 10 and 30, are concerned with recent sediments of the river Nile and those of the Cracow Municipal Water Works. Material pertaining to the montmorillonite group has been mostly taken from a paper by Hendricks and Ross [1] and data of glauconite analyses from Polish literature [3]; the remaining analyses were made by the writer [4], [5]. Owing to restricted space no detailed analytic reports are here published, but only the results of certain calculations made of the mole-percentage of parts dissolved in HCl *). These calculations have yielded suitable parameters as a basis for including the comparative material in a concentration triangle projection and an orthogonal projection, and for plotting a graph illustrating the mole relations SiO_2/R_2O_3 and SiO_2/Al_2O_3 (Figs. 1 and 2). For the triangle projection the mole relations $SiO_2 + Al_2O_3 + Fe_2O_3 = 100$ have been selected, by adding to each point two further (supplementary) parameters in an orthogonal projection, viz., mole per cent of MgO and of alkalies. In this way every analysed element is characterised by the principal oxides, of essential importance in determining the nature of the montmorillonite-glauconite group, at the same time enabling a direct comparison of that group to be made with other soil colloids **).

The analysis table and the projections suggest the following conclusions:

1. In the Si-Al-Fe triangle all the analytic points are dispersed along a line joining SiO_2 and Al_2O_3 apexes. The parameter Fe_2O_3 does not exceed 30 per cent; the montmorillonite and glauconite links have nearly all been shifted in the direction of the SiO_2 apex; the soil colloids have been placed within a field distinctly poorer in this constituent.

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*) Fifty-six complete analyses will be found in Roczn. Nauk Roln. **1** (1957).
**) Fig. 2 does not contain all the points included in the table of analyses.

An intermediary position may here be observed where both groups of minerals grade into each other. Furthermore, the fortuitous dispersion of points within the field of the triangle is almost identical in both groups.
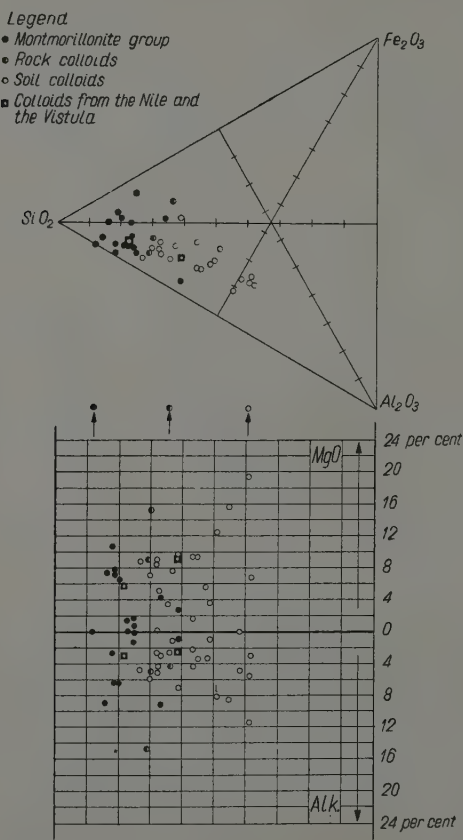

Fig. 1

2. In the orthogonal projection the MgO and alkali values also show a fortuitous dispersions for both groups, without displaying any functional connection with the points plotted in the triangle. The impression is given that, should a sufficient percentage of silica be removed from the montmorillonite and glauconite links, it would be impossible to distinguish in either projection soil colloids from the montmorillonite-glauconite group.

3. In the graph illustrating the mole relations of SiO_2/R_2O_3 and SiO_2/Al_2O_3, all the analyses have been grouped along straight lines.

Montmorillonite and glauconite, with some exceptions, are here distinguished by an obviously higher exponent of the stated relation (from 7.3 to 3.0). The soil colloids occupy lower positions, being arranged in a packed row, with exponents ranging from 2.1 to 0.6. Extracts of Flysch rocks as well as some glauconites and Volhynian bentonite occupy an intermediate position, overlapping with some soil colloids. Bentonite from Lipowica (No. 42) closes the column with the lowest exponent — $SiO_2/R_2O_3 = 0.5$.

4. The numerical data indicate that the chemical composition of that portion of the soil colloids here considered, which were isolated by treatment in 20 per cent hydrochloric acid, agrees with the chemical
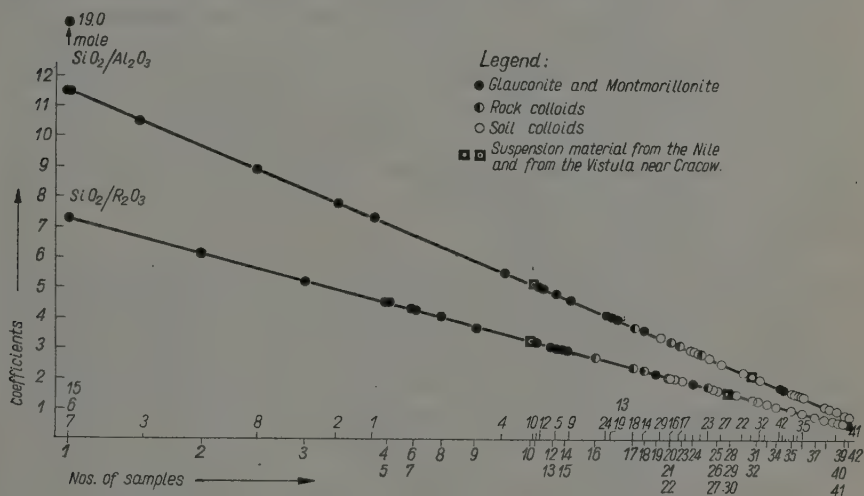

Fig. 2

composition of nearly all the links of the montmorillonite and glauconite groups now recognised. Hence, the conception with regards to the formation of these links within soil profiles is reasonably confirmed by the writer's research work. The removal of the montmorillonite-glauconite links in the direction of higher values of the exponents SiO_2/R_2O_3 and SiO_2/Al_2O_3 may be explained by the process of their secondary silification in marine environment, due to a corresponding geological age (diagenesis).

A comparative table of the analyses made of recent suspensions carried by river waters from different climatic zones to basins of sedimentation, would be most helpful in the solution of this problem. For the sake of illustration two analyses are here given of recent colloids transported to basins of sedimentation. They have been made of the colloidal suspension (particles) of the river Nile, collected near Cairo

and analysed during 1925—1927 [6], also of the colloidal material deposited by the river Vistula on the filtres of the Municipal Water Works in Cracow.

The following numerical data are characteristic of these two materials:

mole (per cent)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	CO_2	SO_3
Nile colloid	44.32	20.63	7.46	3.03	0.50	8.48	9.35	1.23	10.1	0.23	3.03	—
Vistula colloid	40.42	7.79	17.08	—	0.46	12.51	13.50	3.99	3.50	0.46	—	0.29

In order to make possible a comparative study of these two materials, 45 per cent of the arenaceous suspension particles, with size above 1 micron, were substracted from analyses published in Egyptian literature. Upon insertion of corresponding points plotted in the projections of these analyses it has been ascertained that the suspension material carried by the two rivers is distinctly different. The marked differences here observable, particularly with regard to the SiO_2 and Fe_2O_3 content, are undoubtedly referable to differences of climatic conditions prevailing in the basins of the two rivers.

Attempts aiming at a solution of the paleogeographical problem set by this paper have for the time being been confined to the selection of a proper investigation method. No far-going inferences may be made on evidence of the available analytic material. The soundest evidence might undoubtedly be supplied by analysing, according to methods here given, the suspension particles carried to their basins of sedimentation in all the more important rivers of the Globe.

DEPARTMENT OF SOIL SCIENCE, HIGHER SCHOOL OF AGRICULTURE, CRACOW

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TABLE

of analytic projection parameters calculated in mole per cent of extracts in HCl

Columns 1–21

mole per cent	1 Saponite	2 Montmorillonite	3 Glauconite from Bonarka	4 Montmorillonite	5 Bentonite from Chmielnik	6 Glauconite from Mokrotyn	7 Glauconite from Tyśmienica	8 Glauconite from Glińsko	9 Montmorillonite	10 Particles (Material) deposited on filtres of the Municipal Water Works in Cracow	11 Nontronite	12 Glauconite from Sweden	13 Beidellite	14 Montmorillonite	15 Nontronite	16 Montmorillonite from Kobyl, tuffite	17 Colloids from Besko	18 Colloids from Grabowiec	19 Glauconite from Braunfels	20 Alluvial Soil from Goczałkowice	21 Light loam from Mydlniki
Nos. of samples	81*)	4		22					35		57	46	44	47	99					156	
SiO₂	88	86	84	82	82	81	81	80	79	77	77	76	76	75	75	73	71	70	69	68	68
Al₂O₃	12	11	8	15	17	7	7	9	17	15	15	15	19	21	4	23	23	19	17	23	22
Fe₂O₃	0	3	8	3	1	12	12	11	4	8	8	9	5	4	21	4	6	11	14	9	10
MgO	42.0	17.0	7.01	8.6	10.6	7.87	7.48	6.57	7.0	5.5	1.4	2.0	1.6	4.7	0.8	8.7	9.0	15.3	7.0	0	8.2
Alk.	0	0.5	9.05	0	2.8	6.54	6.56	6.15	0	3.1	0	7.6	1.4	1.0	0	4.9	14.7	5.5	6.0	3.0	5.3
SiO₂/R₂O₃	7.3	6.1	5.2	4.5	4.5	4.3	4.3	4.0	3.8	3.3	3.3	3.1	3.1	3.0	3.0	2.7	2.4	2.3	2.2	2.1	2.1
SiO₂/Al₂O₃	7.3	7.8	10.5	5.5	4.8	11.5	11.5	8.9	4.6	5.1	5.1	5.0	4.0	3.6	19.0	3.2	3.1	3.7	4.0	2.9	3.0

Columns 22–42 / A

mole per cent	22 Light loam from Cracow (mean from 10 samples)	23 Alluvial Soil from Goczałkowice	24 Glauconite from Zawichost	25 Colloid from Besko	26 Heavy loam from Cracow	27 Alluvial Soil from Goczałkowice	28 Bentonite from Volhynia	29 Alluvial Soil from Goczałkowice	30 Nile colloids	31 Alluvial Soil from Goczałkowice	32 Alluvial Soil from Goczałkowice	33 Heavy loam from Cracow (mean of 10 samples)	34 Alluvial Soil from Goczałkowice	35 Light loam from Cracow	36 Vistula River sand	37 Heavy sand from Cracow (mean of 10 samples)	38 Pond at Gołyąsz	39 Loess from Mogiła	40 Light sand from Cracow (mean of 10 samples)	41 Heavy loam from Cracow	42 Bentonite from Lipowiec	A
Nos. of samples		8		9b	268	56	41			105	169		153									A
SiO₂	68	67	66	64	64	63	61	61	61	56	56	55	52	51	49	45	42	39	39	38	34	34
Al₂O₃	23	25	16	23	29	25	35	18	29	34	27	35	35	35	33	46	44	45	47	48	56	56
Fe₂O₃	9	8	18	13	7	12	4	21	10	10	17	10	13	14	18	9	14	16	14	14	10	10
MgO	8.2	5.0	4.4	37.1	3.6	7.9	2.6	9.6	9.3	9.3	1.8	9.6	5.8	3.9	12.4	15.7	0	27.4	19.4	6.6	15.0	15.0
Alk.	4.6	3.1	9.5	4.5	2.6	13.0	1.1	7.1	2.8	2.5	4.2	3.4	3.6	1.3	8.1	8.7	5.2	11.8	5.9	3.0	5.5	5.5
SiO₂/R₂O₃	2.1	2.0	1.9	1.7	1.7	1.7	1.6	1.6	1.6	1.3	1.3	1.2	1.1	1.0	0.9	0.8	0.7	0.6	0.6	0.6	0.5	0.5
SiO₂/Al₂O₃	2.9	2.7	4.1	2.8	2.2	2.5	1.7	3.4	2.1	1.6	2.0	1.6	1.5	1.4	1.5	1.0	1.0	0.9	0.8	0.8	0.6	0.6

*) Nos. of samples.

On the Genesis of the Ferrous Dolomites from the Carpathian Flysch

by

W. NARĘBSKI

Presented by M. KSIĄŻKIEWICZ on January 15, 1957

The composition and mineralogical character of concretions appearing in fine-grained sediments are highly valuable indices of the physicochemical conditions of the environment. Pelitic sediments of Carpathian Flysch often contain various formations of this kind. Unfortunately, the only available poor analytical material concerns the Cretaceous siderites and Eocene manganese carbonate concretions. The present paper seeks to establish the mineralogical composition and origin of carbonate layers and concretions appearing in the youngest sedimentary member of Carpathian Flysch — the Menilite-Krosno series (Eocene-Oligocene). It should be noted that the possession of superficial features has caused them to be generally regarded as sideritic marls or even siderites.

Samples of carbonate intercalations from the Menilite shales (Komańcza), the Grybów shales, the Transitory beds (Wetlina) and the Krosno beds (Leśnica) were subjected to chemical, microscopical and differential thermal investigations.

The results of chemical analysis, expressed in percentage molecular contents of Ca, Mg, Fe and Mn carbonates, and the ratio of $CaMg(CO_3)_2$ to $Ca(Mg, Fe)(CO_3)_2$, are presented in Table I. They demonstrate beyond doubt that the formations examined are composed not of siderite but of minerals of the isomorphic dolomite-ankerite series. The differential thermal curves of the samples examined and several specimens from other places, proved to be in complete agreement with the results of chemical analyses. Since the content of $Ca(Fe, Mn)(CO_3)_2$ in the carbonates analysed never exceeds $20-25$ molecular per cent they are not true ankerites and have therefore been named "Ferrous dolomites".

TABLE I

Content of individual carbonates in typical Carpathian ferrous dolomites
(in molecular percentage)

Locality and stratigraphical horizon	$FeCO_3$	$MnCO_3$	$MgCO_3$	$CaCO_3$	$CaMg(CO_3)_2$	$Ca(Fe, Mn)(CO_3)_2$	$CaCO_3$ *)
Komańcza Menilite shales	4.2	0.2	43.6	52.0	87.2	8.8	4.0
Wetlina Transitory beds	5.2	0.1	38.9	55.7	77.8	10.3	11.4
Grybów Grybów shales	7.1	0.5	35.2	57.2	70.4	15.2	14.4
Leśnica Krosno beds	8.9	0.2	40.9	49.9	81.8	18.2	—

In this connection the following classification of this isomorphic series is proposed:

$CaMg(CO_3)_2$	$Ca(Fe, Mn)(CO_3)_2$	Name
100—90	0—10	dolomite
90—70	10—30	ferrous dolomite
70—25	30—75	ankerite

It was shown by J. A. Smythe and K. C. Dunham [3] that ankerites containing more than 75 per cent of ferrous dolomite most probably do not occur in nature.

This division has a genetical justification. Larger rock complexes, being products of lagoonal sedimentation or regional dolomitization consist generally of almost non-ferrous dolomite. The ferrous dolomites of layered and concretionary forms occurring in dark, bituminous shales are most probably a product of early diagenetic changes of sediment (see later discussion). On the other hand highly ferrous ankerites appear almost exclusively in veins of hydrothermal origin.

In opening the discussion on the origin of the Carpathian ferrous dolomites, first should come the general geochemical characteristic of the shales containing them. In order to obtain the necessary physicochemical data, the recently proposed method of determination of various forms of iron in sediments [1], [5] was employed.

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*) the surplus of $CaCO_3$ is connected with secondary calcitic veins, which are characteristic of the specimens from marly shales.

The total amount of iron present in a given sediment is the sum of its several mineral forms; it may be expressed by the equation:

$$Fe_{total} = Fe_{HCl}^{+2} + Fe_{HCl}^{+3} + Fe_s + Fe_{clastic}$$

where:

Fe_{HCl}^{+2} — bivalent iron soluble in 2 per cent HCl (sideritic and leptochloritic),

Fe_{HCl}^{+3} — trivalent iron soluble in 2 per cent HCl (hydrogetitic),

Fe_s — pyritic iron soluble in conc. HNO_3,

$Fe_{clastic}$ — clastic iron insoluble in acids.

The mutual quantitative ratio of these forms of iron depends on *Eh* and *pH* of the medium whereon the decisive infleunce is the organic matter present in the sediment. The prevailing migration form of iron in marine water is pelitic gel of Fe_2O_3. aq., which is deposited together with the fine terrigenic material. This reactive form of iron is subjected to gradual reduction and dissolution caused by bacterial decomposition of organic matter with consumption of oxygen and evolution of chemically active gases (CO_2, H_2S, NH_3). The greater the quantity of organic substance found in the sediment the more reducing medium and the more pyrite is formed at the expense of other forms of iron. Knowledge of the amount of the various forms of iron is therefore of greatest importance since it makes possible an approximate determination of the physico-chemical conditions of sedimentation and especially of diagenesis of a given sediment.

The results of determination of the various forms of iron in a sample of Menilite shale from the top of a dolomitic layer in Komańcza are as follows:

Fe_{total}	Fe_{HCl}^{+2}	Fe_{HCl}^{+3}	Fe_s	C_{org}
1.59	0.09	—	0.31	2.2

It should be stressed that the organic substance shows an increased content of bituminous compounds. As may be seen from the above data the environment of formation of these shales was strongly reducing and therefore, formally, they should be placed in the transitory sideritic-pyritic geochemical facies. It seems, however, that in view of the specific character of such sediments, expressed in a complete lack of authigenic siderite and frequent occurrence of concretionary ferrous dolomites, they cannot be fitted into any geochemical facies hitherto distinguished. Therefore, I propose to name this specific type of sediment as the dolomite-ankerite geochemical facies (or subfacies), the most characteristic features of which can be specified as:

1. Lowered content of total iron due to the small quantity of reactive hydroxide in the parental sediment.

2. Almost complete lack of iron soluble in weak acid caused by hydrogen sulphide (generated from sulphate ions by bacterial action) which reduces to minimum the diagenetic mobility of iron, binding it in the inreactive form of pyrite, and determines the low redox potential of the system.

3. High alkaline reserve and pH of the parental clay solutions connected with the increased quantity of magnesium bicarbonate and ammonia, produced by decomposition of bituminous organic substance, and with the reduction of strongly acidic sulphate ions.

4. Highly increased partial pressure of CO_2 due to rapid bacterial decomposition of bituminous organic substance.

These geochemical features of the diagenesis medium of bituminous shales are most favourable for the genesis of dolomite, and simultaneously exclude the possibility of the formation of siderite. The principal condition of formation of dolomite is the cumulation in a medium, saturated with calcium carbonate, of a minimal quantity of $Mg(HCO_3)_2$. According to O. K. Yanatieva [6], the precipitation of dolomite in fresh water starts from the molar concentration ratio $Mg(HCO_3)_2 : Ca(HCO_3)_2 = 1:6$, and at the salinity equal to 1% NaCl beginning at the ratio $1:9$. This quantity of magnesium bicarbonate is also sufficient for the creation of a suitable high alkalinity ($pH = 8-9$). The increased partial pressure of carbon dioxide has a very important influence on the manner and speed of formation of dolomite. The experiments of A. Rivière [2] have shown that, since during the precipitation of dolomite there occurs an evolution of acidifying the environment CO_2 from decomposing bicarbonates, the presence of a neutralising agent — e. g., ammonia — or a constant removal of carbon dioxide is essential for the continuation of this process. Attention is drawn to the fact that in the case discussed mobile bivalent iron plays, in spite of the small quantity of it in the system, a considerable role. This iron, in view of its close crystallochemical affinity to magnesium, compensates an eventual decrease of concentration of the latter in solutions and stipulates the formation of dolomite distinctly richer in iron than lagoonal dolomites.

The process of formation of the Carpathian ferrous dolomites may be therefore reconstructed as follows. In the upper strata of pelitic bituminous sediment of the Menilite type, cut off from the sedimentation environment, bacterial decomposition of organic substance caused intensive chemical reactions and distinct changes of composition, Eh, and pH of absorbed sea water. Under high partial pressure of carbon dioxide, the clay solutions were enriched in calcium, magnesium and iron bicarbonates. Simultaneously, the concentration of sulphates gradually decreased due to bacterial action; at their expense more and more hydrogen

sulphide was formed, which involved a considerable part of the reactive iron as immobile sulphide. As a result of decomposition of the bituminous organic substance, alkalising ammonia appeared in clay solutions. Compactive pressing out of solutions contained in clays caused the latter to lose the surplus of carbon dioxide on contact with sea water or sand intercalations revealing greatly increased permeability to gases. The rapid loss of this gas and the constant supply from below of almost non-sulphate, alkaline clay solutions rich in bicarbonates, created ideal conditions for the formation of dolomite in the contact area clay-sea water or clay-sand. This process lasted apparently until complete exhaustion of magnesium and of supplementary bivalent iron ions in the solutions migrating to the contact area. The following are indications that in our case a direct precipitation of ferrous dolomite took place:

1. the chemical composition of specimens examined corresponds almost exactly to theoretical dolomite formula;

2. the uniformly grained and very fine crystalline structure of dolomites shows no traces of secondary processes.

To sum up, the direct sources of magnesium for the dolomites discussed should be sought not in the water of the basin but in geochemically changed clay solutions saturating the fine grained Eocene-Oligocene bituminous sediments of the Carpathian Flysch sea. With a view to stressing the specific character of sediments of this type, differing considerably in redox potential, alkalinity, iron content, bituminous character of organic matter and consequently in the mineralogical quality of diagenetic concretions from lithologically similar siderite-bearing shales, it is proposed to give to the former a separate name of dolomite-ankerite geochemical facies (or subfacies).

LABORATORY OF GEOCHEMISTRY, SCHOOL OF MINING AND METALLURGY, CRACOW

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Sedimentary Characteristics of the Flysch-Aalenian in the Pieniny Klippen Belt (Central Carpathians)

by

K. BIRKENMAJER

Presented by M. KSIĄŻKIEWICZ on January 15, 1957

Stratigraphic-tectonic position of the Flysch-Aalenian

The deposits whose sedimentation is discussed in the present paper were known already to V. Uhlig [18]. He referred them to the Upper Cretaceous mantle. This view was initially also shared by L. Horwitz who, however, soon modified his opinion assigning the Flysch deposits considered here to the Barremian-Aptian, and partly to the Albian ("Black Cretaceous") of the Pieniny Klippen series [7]. In 1929, on evidence of Dogger fossils collected from the "Black Cretaceous", D. Andrusov [1] first included this member in the Aalenian-Dogger of the Pieniny passage series, subsequently [2], on specimens of *Leioceras opalinum* (Rein), in the Lower Aalenian. A similar view was also accepted by L. Horwitz [8], [9] when he recognised the "Black Cretaceous" as the Bajocian (Flysch-Dogger) of the Pieniny passage series. The Flysch link of the Aalenian has also been ascertained within the Czorsztyn series [2], [3].

The writer's investigations [4] has led him to conclude that the Flysch-Aalenian constitutes a horizon lower than marls with *L. opalinum* and overlying the non-Flysch deposits (sub-Flysch beds) in the Czorsztyn series, and underlying the Middle Aalenian Posidonomya beds of the Branisko series. Further research studies, however, have shown that [5] the sub-Flysch member and most of the Flysch-Aalenian deposits, initially [4] referred to the Czorsztyn series, belong to the Branisko series. Furthermore, Flysch-Aalenian deposits have also been ascertained within the Niedzica series.

The most complete development of the Flysch-Aalenian is found within the Branisko series (up to 200 m. in thickness). The substratum is here composed of shales with concretions of siderite-dolomite and with

concretions of pyrite without admixture of quartz grains (sub-Flysch beds); in the upper part the shales contain *Posidonomya alpina* (Gras.) The superstratum of the Flysch-Aalenian forms also non-Flysch shale-marly deposits (Posidonomya beds) joined with the Flysch-Aalenian by a transition where shales are intercalated by sandstones (supra-Flysch beds). The Flysch-Aalenian here contains *Posidonomya alpina* and has been referred to the lower part of the Aalenian.

Within the Niedzica series the development of the Flysch-Aalenian is markedly weaker, ranging from 20 to 30 m. in thickness. The contact with the substratum is of tectonic character, *L. opalinum* being recorded from the overlying marls. Within the Czorsztyn series Flysch-Aalenian deposits have been found to occur in one site only at Czorsztyn Castle, 0.5 m. in thickness, underlying the *L. opalinum* marls. No Flysch member has been detected within the Aalenian of the Pieniny series.

The sedimentary characteristics of the Flysch-Aalenian have been studied within the Branisko series only, since there are no adequate outcrops in the other two series. The Flysch-Aalenian, as well as other links within the Klippen belt, are strongly disturbed.

The Flysch-Aalenian of the Pieniny Klippen belt is the oldest Flysch formation within the Carpathians. Its appearance at the beginning of the geosynclinal cycle is not to be associated with any major orogenic phase of regional significance; neither do the over- nor the underlying links display any characteristic of Flysch deposits.

Lithological characteristics

The lowermost part of the Flysch-Aalenian, about 10 m. thick, consist of shales with thin intercalations — from 2 to 20 cm. — of sandy graded crinoidal limestones and sideritic marly limestones. Small limestone and dolomite fragments (resembling Middle Triassic deposits) occur within the crinoidal limestones. Occasionally, the graded crinoidal limestone constitutes the lower part of a layer, passing upwards into marly-sideritic limestones.

The middle part of the Flysch-Aalenian, some 140 m. thick, consists of grey and black, often strongly micaceous shales, ranging from 0.2 to 2 m. in thickness, with intercalations of grey, strongly micaceous sandstones and siltstones, from 0.1 to 1 m. thick. The ratio of shales to sandstones is 5:1, 4:1, and occasionally even 10:1. The sandstones are mostly graded and evenly laminated; diagonal and diagonal-laminated bedding, as also undulated and slip bedding is much rarer. Sandstones are fine-grained, without conglomerates. Organogenic casts on the under sides of the sandstone layers are rare. Flute and groove casts are extremely rare. Small discoidal spherosiderites with a diameter of up to a score cm. occur in shales.

The upper part of the Flysch-Aalenian (about 50 m.) consists of sandstones dominating over shales. Sandstones, with thickness of beds ranging from 0.2 to 4 m., are brittle, fine- or medium-grained; they contain mica and carbonised plant detritus, their colour is light grey or whitish, the bedding graded, occasionally laminated; sometimes they are unbedded. They are weathering to spherical blocks. The shales are grey and greenish coloured, with a thickness from a dozen or so cm. up to 1 m. The ratio of shale to sandstone is 1:2, 1:1.

Allochtonic coal intercalations of the Aalenian age occur within the sandstones of the upper link and the higher part of the middle link.

Types of bedding and hieroglyphs

Within the Flysch-Aalenian, particularly in its middle link, the following types of single bedding have been ascertained: graded, evenly laminated, diagonal, diagonal-laminated, undulated and slip. Furthermore, combinations of single bedding within the same layer constitute composite bedding.

In layers with graded bedding the coarser grade may concentrate near the bottom, gradually diminishing upwards. This is normal, complete graded bedding (Fig. 1). If the upward gradation of grains is not uniform we have normal, incomplete graded bedding (Fig. 2). Within the top part of a layer with graded bedding, shale may occur immediately or, much more often, fine-grained laminae, some over ten in number, either of constant thickness or showing normal gradation (Figs. 2, 4, 5, 7). Symmetric, inverted graded bedding is also observable where the finer grade occurs at the bottom and top parts of layer, with the coarser fraction intervening (Fig. 3). Graded bedding is noted within sandstones as well as within sandy crinoidal limestones. In the latter, segments of Crinoidea behave in a manner highly analogous with that of quartz grains.

Within the type of bedding here studied, the gradation of the grain material is never complete, since in every case, with the main grade, the finer or coarser grade also occurs.

Laminated bedding is second in frequency of occurrence. It may occur independently, but is more often found together with graded bedding. Among the laminated types of bedding those without gradation, uniformly laminated (Fig. 8) are observed, as well as those ununiformly laminated. Much more frequently, however, particularly in the case of laminated bedding making part of composite bedding, the laminae show normal (Fig. 4) or inverted gradation (Fig. 9). In the case of composite bedding, laminated bedding usually constitutes the upper part of a sandstone or siltstone layer; occasionally, however, it may constitute the lower part too (Figs. 9—11).

Diagonal non-laminated bedding is very uncommon in Flysch-Aalenian deposits (Fig. 12), the laminated type being somewhat more frequent (Fig. 13). Undulated and slip beddings occur oftener than diagonal bedding; they may occupy either the upper part of a fine-grained, laminated sandstone layer (Fig. 14) or occur within a layer showing composite bedding (Fig. 15).

The types of graded and laminated bedding here considered are referred to turbidity currents action [16], [13], [6]. They have been recorded from Flysch deposits of Paleozoic, Mesozoic or Kenozoic age [11]—[14], [19].

Within Flysch-Aalenian sandstone layers, wash-outs and other traces of submarine erosion have been ascertained, such as recently studied in similar deposits by Ph. H. Kuenen [15] and M. Książkiewicz [13]. Hieroglyphs are encountered in the Flysch-Aalenian almost exclusively on the under side of beds. These hieroglyphs are of organic origin; hieroglyphs (casts) of inorganic origin are much less frequent. The former occur in the form of rolls, nodes, etc., the latter as flute casts of rare occurrence or still rarer groovings. In these, very exceptionally only, terminations are found with shale fragments similar to those recently described by S. Dżułyński and A. Radomski [6] from Carpathian Paleogene Flysch deposits.

Direction of transportation and origin of clastic material

Direction of transportation of material in Flysch-Aalenian deposits may be determined on sedimentary and paleogeographic evidence. The first group involves studies on the direction of diagonal bedding, on groovings and flute casts, the second group studies on the distribution of Flysch-Aalenian deposits within the initial geosyncline and of the direction of growth in thickness of the sedimentary complex. Owing to poor outcrops and strong tectonic disturbances, measurements of the directions of transportation accomplished by analysing the hieroglyphs and the bedding, are of a cursory nature only. Within the Branisko series — the only one where such measurements are possible — ENE to WSW or NE to SW directions of flow have been ascertained. It has unfortunately not been possible to ascertain whether these directions prevail in the other series too.

Investigations respecting the development and depth of the Flysch facies in Aalenian deposits of the respective Klippen belt series provide more ample information with regard to the origin of clastic material. In the initial geosynclinal Klippen basin the position of the Pieniny series was the southernmost, the Branisko, Niedzica and Czorsztyn series following successively in a northerly direction. No Flysch-Aalenian deposits were recorded from the Pieniny series; within the Branisko series
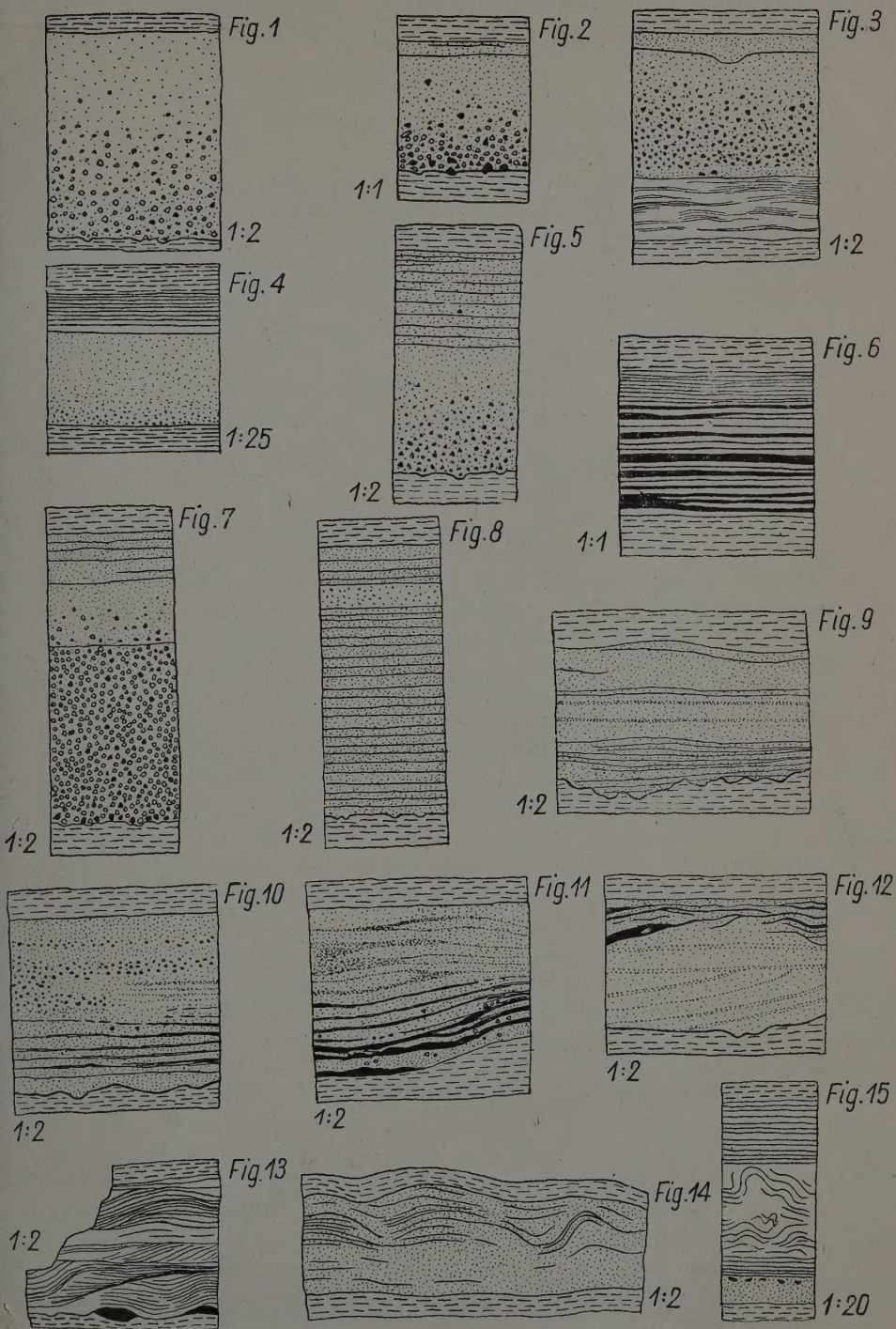
Figs. 1—15. Common types of bedding encountered in sandstones, sandy crinoidal limestones and siltstones of Flysch-Aalenian deposits. Shales indicated by interrupted line; quartz grains and rock fragments by black dots and sharp-edged patches; segments of Crinoidea by sharp-edged, white-centred patches. Lamination indicated by black continuous lines. Description of types of bedding in the text.

they attain a thickness of 200 m., ranging from 20 to 30 m. within the Niedzica series, while in the Czorsztyn series their presence is very uncertain (0.5 m.).

This pattern of the distribution of Flysch-Aalenian deposits here points to their strongest development in the centre of the geosyncline, making quite reasonable the recognition of the presence of a central cordillera (Fig. 16).
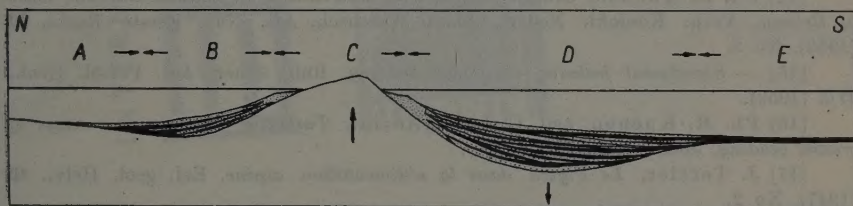

Fig. 16. Reconstruction of the Klippen series geosyncline during sedimentation of Flysch-Aalenian deposits (vertical scale exaggerated). *A*. Czorsztyn series, *B*. Niedzica series, *C*. Central cordillera, *D*. Branisko series, *E*. Pieniny series

Flysch-Aalenian deposits sedimented in the Klippen belt geosyncline long before the commencement of the Middle Cretaceous folding movements within this area. This does not agree with J. Tercier's opinion ([17], p. 181), who believes that Flysch series were deposited only during a period previous to orogenesis. The appearance, on the other hand, of the Flysch facies is associated, as noted by M. Książkiewicz [13], with tectonic activity within the geosyncline.

LABORATORY OF GEOLOGY, POLISH ACADEMY OF SCIENCES, CRACOW BRANCH

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